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A

THEORETICAL AND PRACTICAL TREATISE

ON THE

MANUFACTURE

OF

SULPHURIC ACID AND ALKALI,

WITH THE

COLLATERAL BRANCHES.

BY

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CHAPTER VI.

THE RECOVERY OF THE NITROGEN COMPOUNDS.

THE recovery of the nitrogen oxides which are still present in the gaseous mixture issuing from the last chamber has been previously mentioned as a process indispensable for the rational manufacture of sulphuric acid. It saves not merely at least two-thirds of the nitre, but also a great deal (a quarter up to a third) of the chamber-space; it increases the yield of sulphuric acid, and, moreover, prevents the escape of acid fumes into the atmosphere. Several processes may be employed for this object; but, with one exception, they only require to be briefly mentioned. The only plan which has turned out successful in manufacturing practice, and which, certainly after a considerable length of time, has been introduced into all well-managed works, is that which was proposed by Gay-Lussac as early as 1827, viz. the *absorption of the nitrous fumes by strong sulphuric acid.* The chemical fact underlying this process, viz. the behaviour of the oxides and acids of sulphur and nitrogen towards one another, has been fully discussed in Chapter III. (pp. 212 *et seq.*), to which we must refer. We shall here examine the technical means employed for realizing the possibility of recovering by far the greater part of the nitre contained in the exit-gases from the vitriol-chambers. We recall, therefore, only the following reactions.

Moderately concentrated sulphuric acid absorbs from gaseous mixtures no *nitric oxide* except in the presence of oxygen, when of course higher nitrogen oxides are formed. *Nitrous acid* is absorbed with the formation of nitrososulphuric acid:

$$2\ H_2SO_4+N_2O_3=2\ SO_2(OH)\ (ONO)+H_2O.$$

Nitrogen peroxide is absorbed with formation both of the just-named compound and of nitric acid:

$$H_2SO_4+N_2O_4=SO_2(OH)\ (ONO)+HNO_3.$$

Nitrososulphuric acid is *decomposed* by water alone:

$$2\ SO_2(OH)\ (ONO) + H_2O = 2\ H_2SO_4 + N_2O_3,$$

or by water and SO_2:

$$2\ SO_5NH + SO_2 + 2\ H_2O = 3\ H_2SO_4 + 2\ NO.$$

The most usual *apparatus for retaining the nitrous fumes* by means of strong sulphuric acid is the coke-tower, first proposed in 1827 by Gay-Lussac (who was acting as consulting-chemist to the St. Gobain Company at Chauny), and justly designated everywhere by the name of its inventor. From the facility which this apparatus gives of retaining at least two-thirds of all the nitre, and from the other important advantages realized by it, it might have been expected that it would have been generally introduced within a short period after its invention. But, most curiously, Gay-Lussac's invention was only carried out into practice for the first time in 1842, at Chauny; and forty years after its invention the majority of sulphuric-acid makers did not possess either Gay-Lussac's or any other apparatus for retaining the nitrous fumes; nay, even some of those who had adopted it in the first instance had abandoned it again.

The cause of this was that formerly the only practicable plan of denitrating the nitrous vitriol obtained in the Gay-Lussac tower was by dilution with water, and that the expense of reconcentrating and of pumping the acid, &c., was thought to amount to nearly as much as the saving of nitre. Most manufacturers were not aware that the saving (which was mostly estimated too low, viz. equal to one half of the nitre) was not the only advantage of the absorbing-towers. But the great dearth of nitrate of soda which occurred about the years 1868–70 brought the matter vividly before them; at the same time on the Continent the composition of the chamber-gases, the chamber-space, &c., were studied more closely, and the advantage of an excess of nitrous gas in the chambers, which can only be secured by means of an absorbing-tower, became evident. These circumstances led to the re-erection of Gay-Lussac towers, and the more so as some few manufacturers had never given them up at all and had done very well with them.

In England, where the theoretical part of the subject has been much less attended to, another practical invention had in the meantime been made, which entirely removed the only essential drawback of the Gay-Lussac absorbing-tower, viz. the necessity of concentrating the acid; this was the *Glover tower.* Whilst about 1870 only a comparatively very small number of English works absorbed their nitre-gas at all, since then all the larger and better works have introduced the Gay-Lussac absorbing-tower, nearly always along with Glover's denitrating-tower. Probably some few exceptions may still survive; but we are here only speaking of works somewhat rationally managed.

Gay-Lussac's Absorbing-Tower for Nitrous Gases

consists of a chamber, placed at the end of the set of lead chambers, higher than wide (a "tower" or "column"), of which the walls are made of a material capable of resisting sulphuric acid, and the interior space is filled with a material presenting a large surface. By means of this "packing" a stream of sulphuric acid entering the column from above is divided into small drops; at the same time the current of gas rising up in the tower is divided into many small jets; and thus the contact between the gas and the acid, covering the surface of the packing, is multiplied. The principle applied here is exactly the same that had been employed for a long time in the "scrubbers" of gas-works, in order to deprive the gas of ammoniacal salts by washing it with water, and which is also applied to the condensation of hydrochloric acid in the decomposition of common salt: it is always this, to produce a great many points of contact between the gas and the absorbing agent, and thereby to wash out the absorbable substance of the gas as much as possible; or the interior of the tower may be represented as a filter which allows only the inert gas to pass, but retains the gas acted upon by the absorbing agent.

The reason why such an apparatus is constructed in the shape of a tower or column (that is, why it is made much higher than wide) is this, that in the case of apparatus with a considerable horizontal section it is quite impossible to distribute a comparatively thin stream of the absorbing liquid equally over the whole section, and at the same time to force the gas to meet the liquid all over. Of course, the gas has always a tendency to rise where its progress is not barred wholly or in part by a liquid; unless the towers are pretty narrow, it is not possible to prevent the liquid running down almost entirely in some places, the gas rising in others, so that but little of the two would come into contact, and the liquid would arrive at the bottom charged with very little absorbable matter, whilst the gas issuing at the top would still contain a good deal of it.

Hence follows this general principle:—An apparatus for the absorption of gases, such as those under consideration, should be made no wider than is necessary in order that the draught may not be impeded by the packing; and the necessary cubical volume of the packing should be obtained by making the tower so much higher. Thereby another object is also attained—viz., the gas entering at the bottom of the tower, where it is richly charged with absorbable matter, meets a liquid containing already a good deal of the same, and therefore not capable of dissolving much more, unless an abundant supply is presented to it, which is just the case under these circumstances; on the other hand, the gas near the top of the tower, where it is almost entirely deprived of its absorbable parts, meets entirely fresh liquid, which is able to seize upon those parts even in a poor gas, whilst a partly saturated liquid would have no action upon such a gas. This is the theoretical explanation of the practical fact that a *saturated* absorbing liquid, along with *exhaustion* of the gas, can only be attained by building the towers very high.

A considerable vertical height of the absorbing medium can be also obtained by placing two towers alongside each other, and compelling the gas leaving the first tower at the top to pass downwards in order to rise again in the second tower. As a rule this arrangement is not to be recommended, for two reasons:—first, there is a loss of draught caused by compelling the gas to take the path downwards for a portion of its course, and the consequent great friction in the connecting-tube; secondly, in this way certainly the gas can be completely washed out, but at the same time we do not obtain a saturated absorbing liquid, both of the towers having to be fed with liquid, which at the end only attains *half* the degree of saturation that would have been attained in *one* tower equal in height to both those employed and fed with a single jet. Where the strength of the absorbing liquid is of no consequence, it is often more convenient to employ two towers in series than one of double the height. With the large Gay-Lussac space recently employed by many works it is certainly found impossible to do with only one tower. In that case two towers are employed, the first being fed with the acid run down in the second after pumping it up again. An arrangement decidedly to be rejected is found in many books and in a few badly arranged works, where, from mistaken economy, the absorbing-tower is made of twice the usual horizontal section, and divided into two halves by a partition, in order to pass the gas up one half and down the other. The saving in cost as against two towers or a tower of double the height is not very considerable; on the other hand, that half of the tower in which the gas has to descend is almost entirely sacrificed, because here, where the gas and the liquid travel in the same direction, their mutual action, as experience shows, is very inconsiderable; both mostly travel downwards peacefully without interference and arrive at the bottom almost unchanged. The arrangement of a double tower is inadmissible unless the partition extends right through, and the gas issuing from the one division passes downwards by a special pipe, and is allowed to ascend again in the second division, and thus to *meet* the acid rain. This answers the same purpose as placing two towers alongside each other.

As far as the *width* of the Gay-Lussac tower is concerned, it should be considerably wider than an empty tube of sufficient diameter for the current of gas, not merely because the packing of the tower occupies a large portion of its section and only leaves a small portion of it as clear space, but also because the packing must be purposely arranged so as to divide the current of gas into a great many separate jets, constantly changing their direction, and to expose them to the largest possible amount of *contact* with the surfaces of the packing wetted with the absorbing liquid. The tower must therefore be wide enough to take account of this purposely increased friction. Furthermore, it has to be considered that the *slower* the current of gas, the more time will be afforded for the action of the absorbing liquid, and the more perfect the latter will be. This would lead to giving the tower as wide a section as possible, in order to slacken the speed of the gaseous current. As, for the reasons stated above, this plan cannot be utilized very much, the inference is that a certain middle path should be taken: a tower should be made wide enough not to hinder the draught, and to leave sufficient time for the contact of the gas and the liquid, but not so wide that the liquid cannot be spread equally all over and that the gas can go past it. Evidently no exact calculations can be made as to the proper width; experience only can decide this point. Formerly it was assumed that ordinary coke-packed Gay-Lussac towers ought not to exceed 7 feet in width in order to secure a uniform distribution of the gas and the acids, but latterly towers up to 14 feet have been erected and no drawbacks are reported to have been caused by this extreme width.

The dimensions of the Gay-Lussac tower necessarily correspond with those of the set of chambers to which it belongs; its cubical contents should be *at least* 1 per cent. of the chamber-space. For sets of from 140,000 to 200,000 cubic feet the column might be 6 feet in width and 50 feet high; for a set of from 70,000 to 100,000 cubic feet a tower from 4 to 5 feet in width and 40 feet high is sufficient. In both cases it is best to give the tower an additional height of 10 feet; there will be all the more saving of absorbing acid the higher the tower and the longer the acid has to travel. These statements refer to chambers working with pyrites; with brimstone the height of the tower need not exceed 26 feet.

Undoubtedly a larger absorbing-space, say 2 per cent. of the chamber-space, permits working with a larger economy of nitre than the above-stated sizes; in the case of large sets this space will mostly have to be divided into two towers. In fact, when the absorbing-space at the Jarrow chemical works was raised to 90 cubic feet per ton of pyrites per week, which amounts to about 2 per cent. of the chamber-space, the consumption of nitre was brought down from 1·45 to 1·05 part per 100 parts of pyrites. Similar results have been obtained elsewhere, for instance at Runcorn.

A table of the Gay-Lussac and Glover spaces employed in Lancashire works in 1884 is given on p. 467.

At the Oker works, set No. 1 (p. 462) has three Gay-Lussacs working parallel, each 3 feet 9 inches wide and 32 feet high, capacity 1300 cubic feet = 1·09 per cent. of the cube of the chambers. The other four sets have similar towers, of cubic capacities = 1·30, 1·45, 1·70, 0·96 of the cube of the chambers. They are packed with coke, and are fed with acid of 60° B. = 142° Tw., 100 to 130 per cent. of the daily production. In one case a small plate-tower is also employed as preliminary Gay-Lussac tower, with excellent results (comp. *infrà*).

At the different works belonging to the Saint-Gobain Chemical

Company (the largest in France) the real working-space (*i. e.* that occupied by the coke packing) of the Gay-Lussac towers formerly amounted to rather more than 5 cubic metres (say 180 cubic feet) per ton of pyrites burnt in 24 hours, or from 0·7 to 1 per cent. of the chamber-space. But recently this has been very much enlarged, and now amounts to 13 or 15 cubic metres (say 455 to 525 cubic feet) per ton of pyrites, or from 2 to 3 per cent. of the chamber-space, with a special view to "forced work" (p. 472). This does not comprise the space below the grates, that above the packing, and that occupied by the brick lining, whilst in most other statements the whole space within the leaden shell is included.

The *foundations* of the tower must, of course, be very substantial, and, if possible, constructed in such a way that any acid running over will not damage them. It is perferred to place the towers high enough to avoid the gas from the last chamber having to descend towards the tower ; if, however, the chambers are very high above the ground, this would involve considerable difficulty and expense, and the tower is then raised only high enough above the ground to leave a natural fall from its bottom to an acid-tank, and from this to the pumping-apparatus for the nitrous vitriol.

The foundations usually consist of a solid block of brickwork or stones, or else of two strong pillars surmounted by an 18-inch arch. Sometimes cast-iron columns are employed, on which are placed iron girders, and crossways on these iron T-shaped bearers (usually railway-rails), close together so as to form a continuous platform. These (as well as any brick- or stonework) must be well painted with (frequently renewed) tar-paint, and must be covered at the top by a leaden apron, which directs all the drips past the pillars into a safe place, where the foundations or pillars cannot be touched by it. (The same plan should be followed with the foundations of Glover towers.)

The *framework* of Gay-Lussac towers is sometimes made of angle-iron, but much more frequently of timber. In the case of towers of an angular section such frames are constructed in the usual way, as is seen in our diagrams of Gay-Lussac towers. Circular towers of moderate section are best made with a frame of four uprights, placed in the corners of a square; to these, at every 6 feet of height, metal brackets are fixed; from these are uspended, by means of hooks, broad iron hoops (say 3 inches wide), which closely gird the tower and support its lead shell. Wide towers are built like circular Glover towers (see below).

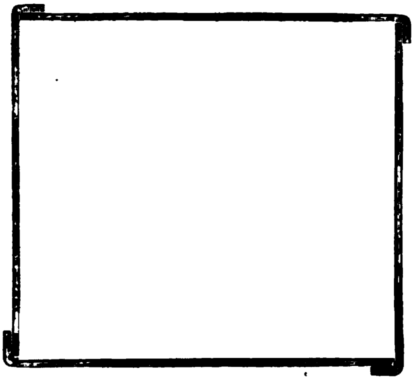
The timber frame must be kept clear of the lead, just as in the case of the vitriol-chambers (p. 428); this, of course, is even more necessary in the case of the Glover tower (see below).

In most cases the Gay-Lussac tower is made of lead. The lead in continental works is often made unnecessarily thick, from 14 to 28 lb. to the square foot; in British works it is often no more than 7 lb. or even 6 lb. to the square foot, like the chamber-lead. It is, however, better to make it of 8-lb. lead, the bottom being a pound or two stronger. There is no reason why the lead should be stronger than this: the gas, as well as the acid, in this apparatus are only moderately warm, and, indeed, should be as cool as possible; nor is the lateral pressure of the coke, if properly packed, so great that it need cause any fear. At any rate the lead sides are necessarily supported by a frame. Both circular and square towers are found; the former take less lead for the same area. They are frequently lined inside with bricks, which are put in dry along with the packing; "split bricks" of 1 inch thickness are often employed for this purpose, lest too much space should be lost. The object of this lining is to prevent the coke from cutting the lead in settling down. It seems hardly worth while to go to the expense of the lining, and at the same time to lessen the area of the tower, for such a small matter, which can be easily remedied by putting on a patch of lead; the lateral pressure of the coke can only be avoided by making the lining 9 inches thick, which is rarely done, as it wastes too much space.

In the case of square towers, the sheets forming the sides should be in one piece from top to bottom. They are best put up by placing the roll of lead on the level of the tower-bottom, unrolling it, supporting the remainder of the roll as it rises upwards and putting the straps in their places as the roll goes up. This is a much safer plan than the other: hoisting the whole roll of lead to the top and allowing it to unroll gradually, fixing the straps all along.

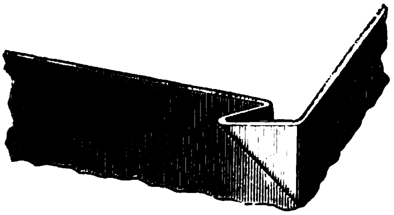
The sheets forming the sides should be turned over at the corners in order to make a joint with the next sheet (fig. 247). The overlaps of the seams must, in every case, be placed outside (also in the case of the Glover tower); otherwise they would be quickly destroyed. The bottom is made of a single sheet, the four edges being turned up to form the upstand. The corners are not cut out and burnt, but are simply folded up as shown in fig. 248.

Fig. 247.



Circular towers are built up of annular drums, one above the other, each being supported by straps nailed to the upright posts, or, preferably, fixed in such a way that the overlap of the seam is turned over three-inch iron hoops suspended from the uprights (p. 581). This plan at the same time protects the hoops and gives an excellent stay to the tower. If there are more than four upright posts, one or more of them must be left out during the building of the tower, to get the leaden drums in.

Fig. 248.



In the south of France octagonal Gay-Lussac towers are in use, built of Volvic lava (see later on), like a hydrochloric-acid condenser, without any lead shell.

All Gay-Lussac towers have an *internal filling* (*"packing"*), which at one time mostly consisted of *coke*. This material was formerly regarded as the best for this purpose, because its irregular shape and rough surfaces offer to the gas a very large area of contact with the liquid. An advantage which coke also has over other materials, as pieces of glass, earthenware, flints, &c., is its comparatively light weight. But two other advantages sometimes claimed for it, viz. porosity and resistance to chemical action, are non-existent. The contention that coke, owing to its porosity, offers a great many internal surfaces for the contact between the gas and the liquid is erroneous. In the first place, porous coke is worthless for a coke-tower, for which dense coke is indispensable; secondly, the pores would at once be filled with liquid, which thus would not come into contact with the gas passing outside. It is not owing to its porosity, but to its rougher, more irregular, and therefore much larger surface, that coke is preferable to broken glass or earthenware, &c.

It is necessary to be very careful in the selection of the coke. Gas-coke is of no use at all here, only the hardest-burnt oven-coke, giving a clear ring and as little porous as possible, of a silvery white, not of a dull black. It must be carefully packed and all dull black pieces rejected. First only the large pieces, a foot and upwards in length, are picked out; these are placed in horizontal layers directly over the grating of the tower, crossing each other if possible; each piece must be placed by hand, inconvenient as it is that the workman has to be lowered down from the top to the bottom of the tower, and must receive his material in the same manner. Thus the first third of the tower is packed; then come the pieces next in size; and for the last third the smaller lumps may be used, and may be simply emptied in out of baskets. Nothing, however, is allowed to go into the tower which has not been sifted on a riddle with three-inch holes. Unless a coke-tower is packed most carefully, either the draught through it will be impeded, or there will be too much way left for the gas, or, in the most frequent and worst case, the packing will be too loose in some places and too dense in others, and thus there will be bad absorption along with bad draught.

Soft porous coke has to be rejected for two reasons: first, it cannot support the pressure of the superjacent column without being crushed, thus stopping the draught; secondly, such soft coke is soon acted upon by nitrous vitriol, and is eventually converted into a thick paste; this is very bad for the draught, and may necessitate repacking the tower. It also imparts a dark brown, at first nearly black, colour to the acid run through the tower for a considerable time (several months) after a tower has been freshly packed.

The claim formerly made for coke, that it is not acted upon by the gases or liquids within the Gay-Lussac tower, must be declared untenable even for the hardest-burnt coke, since I have shown (J. Soc. Chem. Ind. 1885, p. 31) that the reason why "nitrous vitriol" never, except under totally abnormal circumstances, contains any nitric acid, even when the gases entering into the tower had contained N_2O_4, is this, that the coke reduces the nitric acid originally formed from the N_2O_4 to nitrososulphuric acid ; this takes place slowly at ordinary temperatures, but very quickly and completely at slightly higher ones (30° to 40° C.).

In a subsequent investigation (Zeitschr. f. angew. Chem. 1890, p. 195) I have shown that the action goes further, and that nitrous acid is reduced by the action of coke to nitric oxide, with formation of carbon dioxide. It is true that at the ordinary, or at a slightly raised, temperature this action is only very slow; but even then it is quite perceptible, and at temperatures above 70° it becomes very strong (comp. p. 231). This no doubt accounts for some of the losses in the manufacture of sulphuric acid, and it would seem to speak in favour of employing a description of packing which is not acted upon by the nitre in any way. In fact, at some works the ordinary coke-towers must be repacked every year, and in places where the coke-packing has been replaced by cylinders of hard stoneware, the nitrous vitriol is very much stronger than with coke-packing under similar circumstances.

Hallwell (Chem. Zeit. 1893, p. 263) noticed a distinct saving of nitre when he replaced the coke-packing by stoneware.

Of course, dense coke is less acted upon than porous coke (as distinctly proved once more in my experiments); the latter does not even resist the action of pure concentrated sulphuric acid without disintegration. But in the end all coke is gradually wasted, and long before this is done to such an extent that the real loss of weight would make it necessary to replenish the tower, the mud formed by the disintegration of part of the coke stops up the draught to an intolerable extent. Flushing the tower with water is sometimes a remedy, but is far from being always efficacious.

In the case of very tall towers, sometimes one or two grids are interposed at various heights for supporting the upper layers of the coke. These grids are made of iron bars cased in lead. Unless they are very carefully arranged, as will be shown in our drawings, they may go down with the coke packing, as the latter gradually sinks down, and may do more harm than good.

The drawbacks notoriously existing in the case of coke-packed Gay-Lussac towers have long since led to the employment of other styles of packing; short *cylinders of acid-proof stoneware* are mostly used, of which we shall speak in detail when describing the Glover tower. Other stoneware bodies, as Guttmann's or the Bettenhausen balls or cones (p. 500), are equally used.

Comp. also the stoneware apparatus of Kypke (G. P. 97,208) and of the Friedrichsfeld ceramic works (G. P. 89,025); Fischer's Jahresb. 1898, p. 327.

The Rhenania works at Stolberg, when packing Gay-Lussac towers with cylinders alone, found that the stock of acid was not sufficient to provide for irregularities of work. They find it preferable to combine cylinder with coke packing, the former at the bottom, the latter in the upper part of the towers. If the pieces of coke are not too small, there is no stopping up by mud, and such a tower may go for many years (information received in 1902).

An exceedingly suitable apparatus for this purpose is the *plate-tower,* described p. 487 *et seq.* Lüty (Zsch. angew. Chem. 1897, p. 485) gives reports from eleven various firms, in Germany, Austria, England, America, and Russia, which have erected plate-columns as Gay-Lussac towers and which are perfectly satisfied with the results. Niedenführ (Chem. Zeit. 1897, p. 20) quotes reports from factories, showing that the loss of draught with plate-towers is much less than with coke-towers (only 1·5 mm.), and that the former, if combined with the latter, work with less nitre and more acid production than coke-towers alone, especially by the equalization of disturbances in the work.

A very good plan, where several sets of chambers are at work in the same factory, is to provide each set with a first Gay-Lussac tower in the shape of a "Lunge tower" and to convey the gases from all these into a large central coke-tower; the large quantity of weak nitrous vitriol employed in the latter is then employed for feeding all the plate-tower Gay-Lussacs of the individual sets (comp. p. 603, the Griesheim system of centralizing the Gay-Lussac towers). In this case the action on the coke is altogether insignificant, owing to the low temperature and the slight amount of nitre in the central coke-tower.

A Lunge tower of 15 or 20 feet does the same work as a much wider coke-tower of 30 or 40 feet, and causes only a quarter or a sixth of the loss of draught produced by the coke-tower (Niedenführ, 1902).

The combination of plate-towers and a large central coke-tower has the further advantage that any inequalities of work are thus made practically harmless, and the only real objection to plate-towers, viz. the small stock of acid which they contain, is thus completely avoided. As these towers are so low, it will be possible in most cases to place their tops at a slightly lower level than the bottom of the coke-tower and to feed them directly with the acid running from the latter without the necessity of again pumping up the weak nitrous vitriol.

Among English acid-makers, coke-packing seems to be still preferred to all others, as shown by an enquiry made in 1900 by Messrs. P. Spence & Sons (Chem. Trad. Journ. xxvii. p. 262); but their reasons are not very conclusive, and the just-mentioned firm has itself decided for an improved brick packing. No doubt some of the towers packed with bricks or cylinders have not answered their purpose, because the packing was too loose and nothing like as efficient for surface contact as coke packing; but long experience has now shown that the latter, whose chemical drawbacks have been pointed out before, can be replaced by chemically indifferent stoneware, if moulded into proper shape ("Lunge plates," "Guttmann balls," &c.), and that in this way the towers can be made very much smaller than coke-towers, one-sixth to one-tenth or even less.

Repacking Gay-Lussac towers.—Coke-towers, owing to the above-described circumstances, must be emptied and repacked from time to time. This must be done with great care, on account of the nitrous gas present in the towers, which is very poisonous. Since accidents have happened through the gases remaining in the tower, official rules have been laid down in Germany, of which the principal points are the following:—Before repacking is commenced, the tower must be completely disconnected from the chambers, but the connection with the chimney must be left open. The tower must now be washed first with sulphuric acid, then with water or steam, until the liquid running off tests at most no more than 3° Bé. (1·022). During the taking-out of the coke there must always be draught into the chimney: when unpacking from below the draught should act from the top; when unpacking from the top the draught should act from the bottom. If this cannot be done, the cover must be removed and a large hole cut in the side at the bottom. Towers packed with coke must be unpacked from the side and from without, in the case of tall towers on different levels. The packing material must be immediately removed. The workmen must be provided with mouth-sponges, respirating-apparatus, india-rubber gloves, &c. Before removing the mud collected at the bottom it must be stirred up from without with water, and this must be repeated if nitrous vapours are evolved. Men suffering from lung- or heart-disease should not be employed in this kind of work.

The English Alkali Report, No. 31, p. 90, mentions a fatal accident which occurred in repacking a well-washed and unpacked Gay-Lussac tower, and which was evidently caused by the nitre-gas retained by the old brick-lining. It is therefore recommended to ventilate the towers in all cases from the top downwards during unpacking and repacking.

Special rules have been more recently officially laid down in Germany for repacking Gay-Lussac and Glover towers (Chem. Ind. 1897, p. 365).

The 'Chemical Trade Journal,' published at Manchester, supplies posters for fixing up at chemical works, containing *Rules for Dealing with Dangerous Gases,* of which the following is an abridged abstract.

No person may enter a boiler, tank, drain, vitriol-chamber, or tower, except provided with a suitable respirator in good condition. If the gases cannot be absorbed, the men must be provided with a face-piece supplied with air or oxygen. They must be secured round the waist by a rope, and a man must be in attendance to render assistance if necessary. If a man is "gassed," he must be speedily removed into the open air, and placed in a warm, well-ventilated place. In bad cases an oxygen bottle (never to be used without a reducing-valve !) and lung exercise must be employed.

If the man is conscious, the valve is very slightly turned on and the oxygen introduced into his mouth by a glass tube. If unconscious, the tube is put in one corner of the mouth, closing the lips round it and producing artificial respiration in the usual way; if the teeth are set, put the tube in one of the nostrils. The "lung exercise" (described in detail in the "Poster") is the same as that used in the case of accidents by drowning; it is not often necessary.

Complete design of a Gay-Lussac Coke-tower.

In our second edition, pp. 520–523, a description and illustrations are given of a Gay-Lussac tower, as functionating at Freiberg many years ago. In lieu of this we shall here give a design of a modern coke-tower, as carried out by H. H. Niedenführ, figs. 249 to 253. Fig. 249 is a sectional elevation, fig. 250 another at right angles to it, fig. 251 a sectional plan on the plane EF, fig. 252 on the plane GH, on a scale of 1 : 100, and fig. 253 a plan of the network below the saucer.

The tower stands on strong brick pillars (or else cast-iron columns), with an arched top. Above this follows a hollow network *x* of acid-proof brickwork, serving as cooling channels for the wooden floor *z*, the outside of which is provided with the circular lead spout *y*, which keeps any acid running over away from the foundations. Six wooden uprights, *w w*, form the scaffolding for the leaden shell of the tower; they are tied at top and bottom by cross pieces, *v v*, forming a hexagonal frame. Cast-iron brackets fixed in *w w* support the lead sides of the tower, keeping these at a distance of 1 inch away from the wood.

The bottom of the tower is formed by a lead dish, *u u*, with a margin 6 inches high; this is made of lead 6 mm. thick = 14 lb. to the square foot. The sides and top are made of lead 3 mm. thick = 7 lb. to the square foot. The inside of the tower is lined at the bottom, up to the top of the grate, with 13-inch brickwork, above that 7 feet high with 9-inch brickwork, above this 12 feet high with 4½-inch brickwork; the remainder of the shell up to the top has no lining. The lining is everywhere kept an inch away from the lead.

The lead bottom is protected by thin acid-proof slabs. On these are erected pillars, *a*, *b*, which carry the stoneware grids *c*, *d*, each consisting of three pieces, supported by the recesses of the pillars as shown in the drawing. These bearers are 5 inches wide, 16 inches high, and leave open spaces, *e e*, between them, 7 inches wide. They are bridged over by the bricks, *g g*, which support the packing formed of cylinders, to a height of 7 feet. The cylinders (about which comp. p. 586) are placed as shown in fig. 251, so that each of them stands on the crossing-point of four other cylinders. On the top of this packing there is a lead-covered cast-iron grid, *h h* (40 × 100 mm.), upon this 12 feet high of coke-packing, then another grid, *i i*, and again nearly 12 feet coke-packing. The top is formed by a shallow lead dish 5 mm. thick, 2 inches deep, with a number of acid "lutes," *k k*, sealed by small cups, and fed from the long spouts, *l l*, which have as many lips as there are lutes to feed.

This tower is 9 ft. 4 in. wide and 41 ft. high within the lead; the inlet and outlet pipes are 25½ inches wide each.

Falding (Min. Ind. vii. p. 691) gives a design of a Gay-Lussac tower which does not essentially differ from the above.

Both the inlet and outlet pipes of the Gay-Lussac should be provided with a contrivance for *the observation of the colour of the gas* before and after its passage through the tower—say, two glass panes placed opposite to each other; or a portion of each of the two pipes may be made of glass. The gas ought to be of a ruddy colour before entering the tower, and perfectly colourless after leaving it. It is a very good plan to make the "sight" in the shape of a narrow lead box, 6 or 7 feet long, with glass panes at the opposite small ends. In this case the colour is seen through a deep layer of gas, and any admixture of yellow vapours is much more easily discovered than with the ordinary small sights.

Other Nitre-recovery Apparatus on the same principle as that of Gay-Lussac.

Instead of the Gay-Lussac tower in some works, but rarely in large ones, and altogether only exceptionally, absorbing-apparatus composed of *Woulfe's bottles* are used. Two different arrangements of this kind, which are quite obsolete now, are described and illustrated in our first edition, pp. 401 to 403.

More important than this are the proposals to retain the form of an absorbing-tower or column, but to make them in a cheaper or else in a more rational way than the ordinary large coke-tower. In our first edition (pp. 377 and 378) two such arrangements are illustrated, both of them consisting of stoneware pipes; but it is useless to repeat their description here, as they have not been practically tried or else act too imperfectly.

Fig. 254.

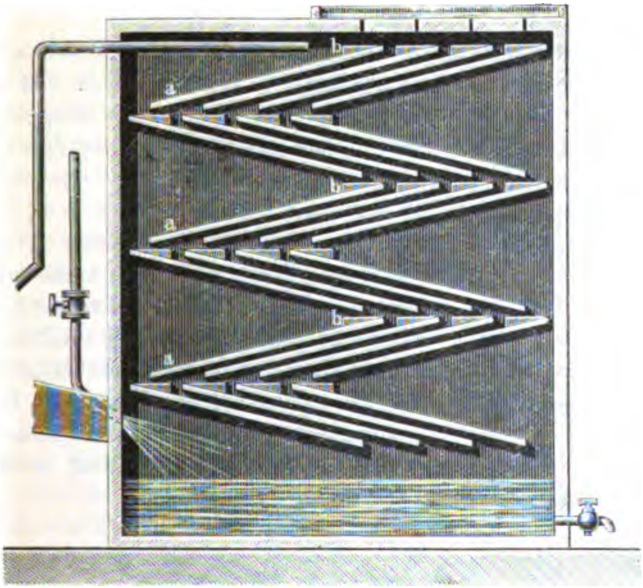
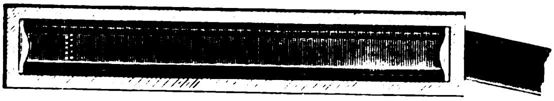


Fig. 255.



A very useful addition to Gay-Lussac towers, especially where they are not sufficiently large, was contemplated by the apparatus invented by F. Benker, and patented by the Soc. An. de Produits Chimiques de Javel (E. P. 10,871, of 1884; J. Soc. Chem. Ind. 1885, p. 456). A small lead tower is placed in the way of the gases before entering the ordinary Gay-Lussac coke-tower. On its bottom there is a grid, covered with a little coke, merely to distribute the gases. On the top there are several spray-producers, of the shape shown on p. 540, fig. 227, made of platinum, by which a fine rain of sulphuric acid is produced in the tower. The gases passing through it yield up a large portion of their nitrous acid, so that much less work remains for the Gay-Lussac tower to do. This plan has been tried at several works, but with only moderate success. Probably the acid-drops fall down too quickly, before the gases have had sufficient time to act upon them.

The apparatus for absorbing gases by liquids, patented by Hoffmann and Carlisle (G. P. 48,283), is shown in figs. 254 & 255. It consists of a column or tower, fitted with groups of spouts, *a a*, inclined in opposite directions, in connection with overflow vessels, *b b*. This apparatus is also intended to make sulphuric acid from sulphur "evaporating" at the same time with nitric acid, both of them being forced into the apparatus by an injector, while the "spent gases" are forced back by another injector into the sulphur-chamber. It is not stated what material this apparatus is to be made of, and the very curious proposal for making sulphuric acid last described will suffice for judging of its technical value.

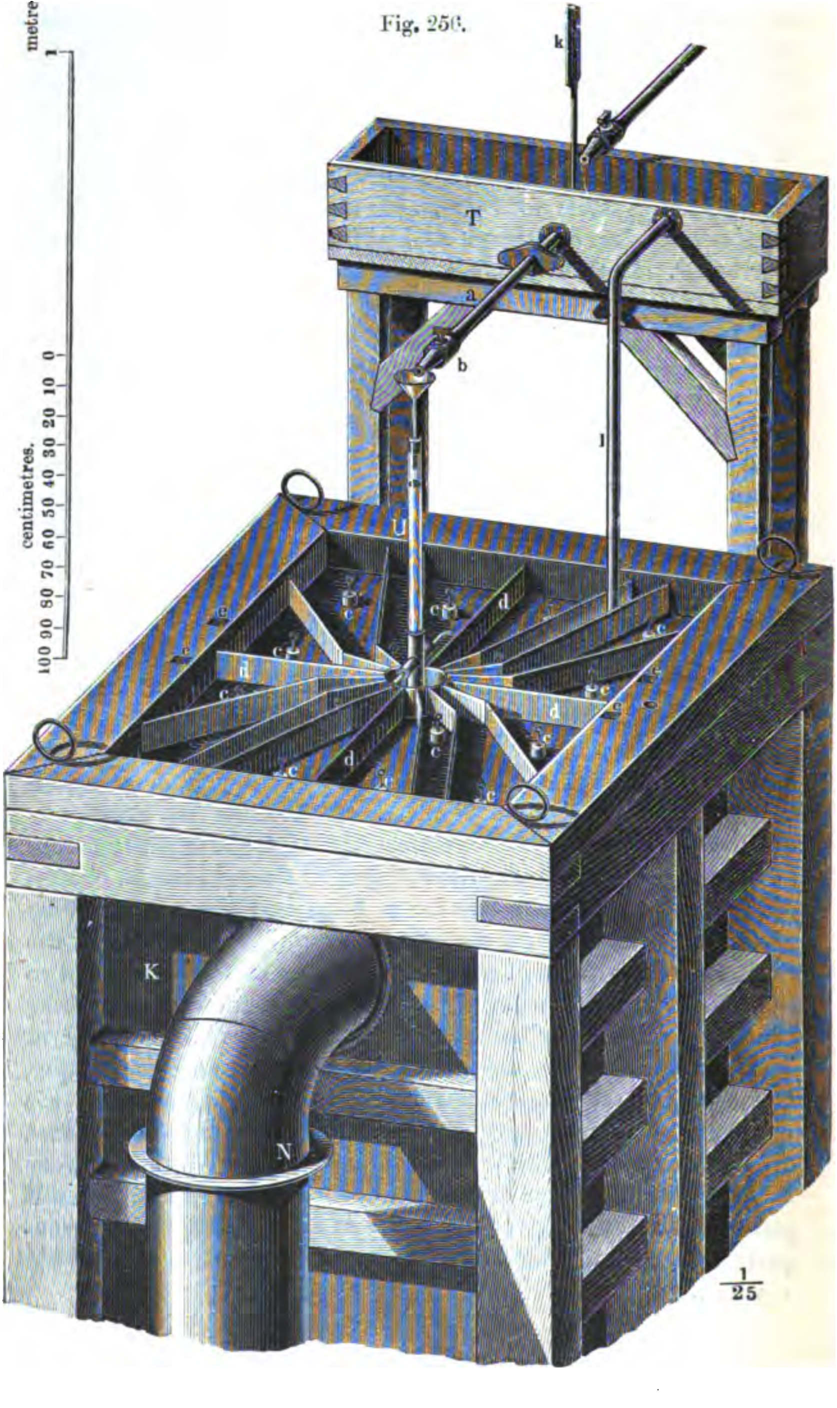
Very similar to this is the apparatus of Izidore & Biscons (E. P. 19,907, 1898), which contains inclined channels attached to the sides of a chamber through which sulphuric acid is run for the purpose of absorbing the nitrous vapours.

Distribution of the Feeding-acid.

In this process it is of great importance that the supply of sulphuric acid, which is to deprive the gases of their nitrous acid, be exactly regulated, and that from the beginning this acid be spread equally over the coke; otherwise too much sulphuric acid may be used, and yet the gas may pass through the tower without giving up the whole of its nitrous acid. Special care must therefore be taken in the construction of the apparatus for spreading the acid. At one time this was performed by a number of small taps which evidently cannot be regulated for a very slight flow without danger of being stopped up, or by "tumbling boxes" and the like.

A much better arrangement is shown in figs. 249 & 250; substantially the same as will be described later on. We shall here describe another arrangement for distributing the acid, which was originally applied at the Aussig chemical works by Mr. Schaffner, namely the *acid-wheel.* In this the supply of acid is regulated by a single tap, which can be opened wide enough to prevent it being so easily obstructed as the sixteen small taps in the former arrangement. Fig. 256 represents this apparatus on a scale of 1 : 25. In the top of the tower there are sixteen holes, *c*, through which the acid trickles on to the coke below. Each hole has an upstanding rim about 1¼ inch in height, which is covered by a lead cap, nicked at the bottom in a few places to the depth of ¾ inch, so that the acid can pass through without hindrance. As soon as the top of the tower is covered with acid to the depth of that rim, the acid runs over into the inside of the tower; but no gas can escape through the holes, as they are luted with acid. The spreading of the acid is effected by a small reaction-wheel U, fed from the tank T by the tube *a* and the tap *b*, which regulates the supply. The lower part of the wheel and the two arms consist of lead; in this is fixed above a strong glass tube, and below another short glass tube, drawn out to a point which runs in a socket of glass or lead. One of the arms is also fitted with a glass tube, from which the acid runs out. There is a guide, consisting of two paralled rods of lead or of wood covered with lead, which rest on frames fixed in the holes *e e* of the top-frame, and on which four glass tubes are placed close to the upright column of the apparatus, so that they form a square within which the column revolves. As soon as the column is filled with acid, the wheel revolves regularly, the liquid running out of the open arm. On the quantity of the acid run in depend the height to which the column is filled and the velocity of its revolution. The axle of the wheel is exactly in the centre of the tower; and a cylinder of lead about 4 inches in height is burnt to the top of the tower, so as to prevent the acid from getting to the centre. From this cylinder sixteen radial ledges *d*, also made of lead and burnt to the top-lead of the tower, branch off at equal distances. These are continued in a straight line as far as the periphery of an imaginary circle, beyond which the wheel cannot discharge any acid, and then alter their direction; so that between each two of them one of the above-mentioned sixteen holes is placed. Thus the top of the tower is divided into sixteen compartments, each of which contains an opening for running off the

Fig. 256.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acid, and all of which are fed by the wheel with an equal quantity of acid.

In England the spreading-apparatus is generally made altogether of lead; we shall, further on, give a drawing of such a spreading-wheel in the description of the Glover tower.

Since it happens now and then that the reaction-wheel stops, especially with a small feed of acid, the arrangement of Seybel, at Liesing near Vienna, can be recommended, by which the wheel at each revolution strikes against a bell audible from below.

Even the best-constructed acid-wheels are liable to get stopped now and then, and this sometimes causes a great deal of trouble if it is not at once perceived, as the tower then ceases to work properly and much nitre gets lost. Hence a new system has been pretty generally introduced, which works quite as well as the acid-wheels, without a mechanical movement liable to get disturbed. It consists in running the acid into a vessel provided with a number of *overflows* kept exactly at the same level, each of these communicating with a separate pipe which leads the acid into the tower. This system can be carried out in a variety of ways, one of the best of which is shown in fig. 257, as seen from above, fig. 258 in transverse section, fig. 259 in perspective view, with the sides partly cut away. From the top *a* the liquid runs into the central vessel A. The cover *b* is not exactly necessary, but is best provided, and is made loose, so that the interior of A is easily accessible. The cylinder A is nicked at the bottom, so that it communicates with the wider but lower trough B. This is provided all round its circumference with overflow-lips (*c c*), which may be close to one another; sometimes 30 or 40 of these are made. They must be arranged in such a way that when B is once filled, all the overflows, *c c*, function precisely alike; this can be easily attained by dressing the lead of the lips a little up or down, as the case may be. Once right, they always act in the same manner. The trough B is surrounded by the wider trough C, which is divided into as many cells as there are lips in B. Each cell is independent of its neighbour; but the partitions, *e e*, are cut out on the top, so that, in case of the pipe of any one cell getting stopped up, the liquid overflows into the next cells. Each cell is also provided with a separate pipe *d*, made tight in its bottom, and hydraulically sealed either there, as it is shown in the diagram, or else on or within the tower. The whole is generally, with Gay-

Lussac towers always, made of lead, but it may also be made of earthenware, iron, or other material suitable for any special case.

Briegleb (G. P. 10,386) has constructed a distributing-apparatus consisting of a cone made of regulus metal, on the top of which a

Fig. 257.

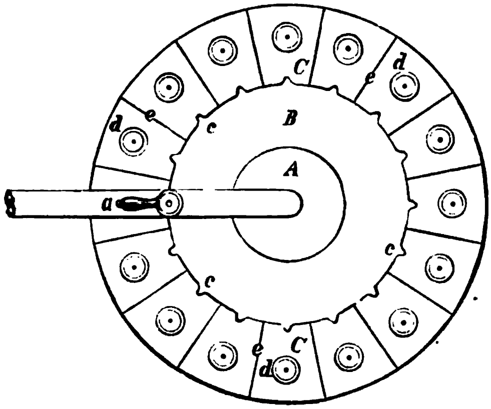
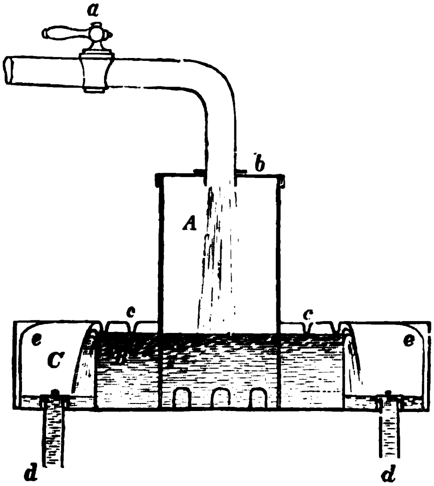


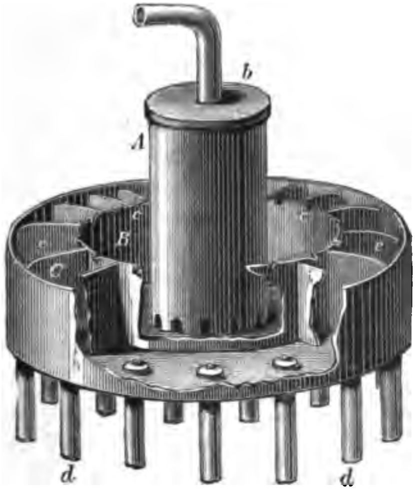
Fig. 258.



jet of acid is directed. The upper part of the surface of the cone is plain, but the lower part is fluted, so that the acid is distributed into a number of jets which are caught in a circular vessel surrounding the base of the cone, and are separately carried away by pipes. No doubt this apparatus can be made to work properly, but it is much less easily kept in order than the simple overflow apparatus shown on p. 578.

In the case of towers of great horizontal section, where the number of pipes coming from the distributor is inconveniently large, much may be saved by employing only one pipe to every four holes on the top of the tower, each pipe ending over a small trough placed at the point of intersection of the lines connecting these four holes; these small troughs will then empty their contents simultaneously into all the four holes. Of course the same precautions have to be taken for securing an equal flow into all the four holes as mentioned in connection with figs. 257 to 259.

Fig. 259.



A very ingenious, but somewhat complicated distributing-apparatus, in which a mechanical revolving drum is employed, is described in the patent of Brock and Saye (No. 11,492 of 1885; J. Soc. Chem. Ind. 1886, p. 487).

The working of a column (whether it be a Gay-Lussac, or a Glover tower, or a hydrochloric-acid condenser, &c.) is, of course, all the more efficient the more uniformly the feeding-acid is distributed over its whole area. It is equally self-evident that towers of a large horizontal section require more feeding-places than narrow ones. It may be laid down as a general rule that there ought to be no smaller number of distributing-pipes than one to each superficial foot of the cover of the tower; but this is a minimum which is greatly, and no doubt advantageously, exceeded at many works.

The *regularity of the supply of acid* to the coke-tower is of the utmost importance for its good working. The whole acid-chamber process is so constituted that its course must be kept as continuous and uniform as possible, and the large bulk of the lead chambers in this case serves as a regulator, similar to the air-vessel of a blowing-engine, so that the gas, on leaving the chamber, issues, or at least ought to issue, with nearly absolutely uniform speed and composition. In similar intervals of time there will therefore be a similar quantity of nitre-gas leaving the chambers; and this in the absorbing-tower should always find the same quantity of acid, lest either there be an escape of nitre-gas or the nitrous vitriol come out too weak. But if the acid flows out of a tank, the opening of the tap remaining the same, the flow will be much quicker at the beginning, when the tank is full, than afterwards, when it is partly empty, and the tower will thus be fed very irregularly. The speed of outflow of liquids decreases in the proportion of the square roots of the heights of liquid in the tank; for instance, when the tank is filled to the height of 4 feet, the flow of acid will be twice as fast as when it only stands 1 foot high—both being cases which often happen in practice.

In order to secure a very regular supply of absorbing-acid to the tower, several arrangements have been adopted,—for instance, Mariotte's vessel (page 517) or the apparatus shown in fig. 260. The vessel Z is placed with its mouth downwards in an open basin E, in such a manner that its mouth is luted by the acid contained in the basin; therefore nothing can run out of Z. But as the acid runs away from E through the pipe *b* on to the coke-tower, the level of E is lowered, the mouth of Z becomes free, a few air-bubbles enter, and acid flows out till the original level is reached, and the mouth of Z is luted again. The valve *d*, with the valve-rod *c* passing through a stuffing-box, serve for closing the mouth of Z during the time that this vessel is being fed through *x*.

In a simpler shape the same principle used to be applied a number of years ago in a few English alkali-works, as shown in fig. 202, p. 531 of our second edition, under the name of "vacuum retorts," which have been abandoned as being too troublesome to keep in order. Very efficient is the balancing-apparatus, fig. 261, A is the large acid-tank on the top of the coke-tower, made of wood lined with lead, which is filled from time to time. Beside it stands a lead cylinder B of equal height and 12 inches wide; the two communicate at the bottom through the lead pipe *a*. This pipe ends in A with a valve-seat *b* of hard lead, bored out in a taper

Fig. 260.

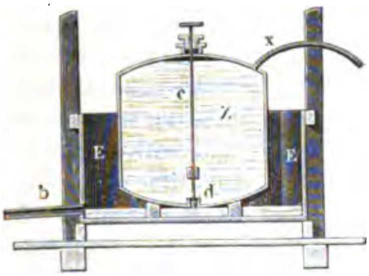
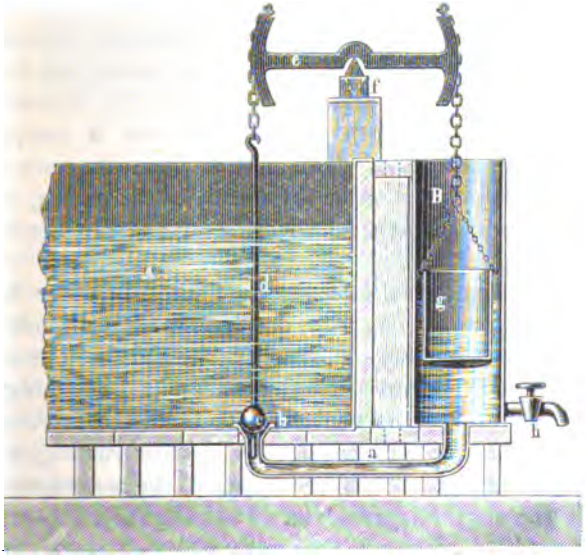


Fig. 261.

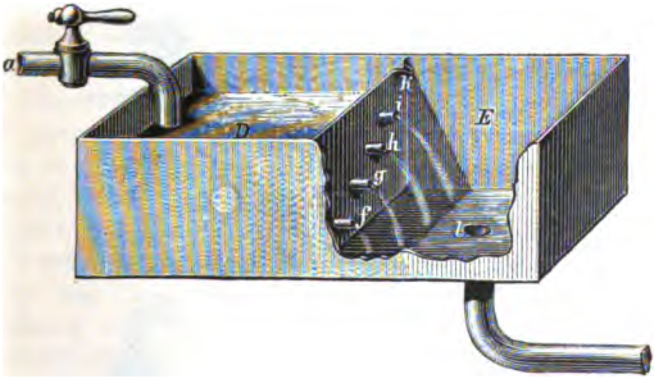


shape. In this plays a ball-valve *c*, also made of hard antimonial lead (" regulus "), which is continued below into a small guide-rod, and above into the lead-covered iron rod *d*, which projects above A, and is suspended by a short chain from one arm of the balancing-beam *e*. The latter swings with its centre on a steel edge *f*, and carries on its other arm, exactly over the cylinder B, another chain, from which a leaden bucket *g* is suspended inside B. Acid is poured into the bucket *g* until it sinks to a certain depth in the acid standing in B; by pouring in more or taking out some of the acid in *g* that depth, and with it the height of acid in B itself, can be regulated at any time: this bucket is therefore a form of float, preferable to the solid lead float figured by Schwarzenberg. The bucket *g* is so weighted, and the length of the chain such, that at a certain height of acid in B the valve *c* must close the opening *b*. The valve *c* with the rod *d* and its chain is about as heavy as the float *g* along with its chain, and closes the opening *b* so long as a portion of the weight of *g* is neutralized by the upward pressure of the acid in B. As soon, however, as the cock *h* begins to run and the float sinks down, the rod *d* is raised by means of the beam *e*, and the ball-valve *c* leaves the opening *b* free; thus acid flows across into B through *a*, lifts the float *g*, and *c* sinks down into its position, closing *b* again. Thus, by small oscillations of *e*, always the same quantity of acid will run out of B in the same time, as this only depends on the weight of *g* and the length of the chain, but is independent of the level of the acid in A. The ends of the beam *e* are shaped as segments of a circle, in order (by means of the chains) to convert their circular movement into a rectilinear one for the rod *d* and the bucket *g*.

The above apparatus, as formerly figured in other books and as employed in many factories, does not work well, and has even been given up in many places where it had been erected. In the first place, the beam is usually represented swinging on a pin which passes through its centre; but then the friction is very great, and soon becomes greater by the iron rusting, so that the beam sticks fast. This cannot happen if the arrangement is that shown in the above diagram, viz. a steel edge like those of delicate balances; when strongly plated with nickel it remains free from rust. But, above all, the valve *c* ought not to be a truncated cone, as it is generally represented, but it should be ball-shaped.

The guiding by the arc-shaped arms of the beam is not so absolutely vertical that a conical valve could not now and then jam itself in its seat during its play upwards or downwards; in that case the apparatus ceases to work. If, however, the valve is ball-shaped, a slight deviation from the vertical does no harm, as the ball always closes the hole, and jamming fast is out of the question. Whilst those manufacturers who had erected the above-mentioned imperfect apparatus were mostly induced to give it up again on account of its constantly breaking down, the arrangement figured here works with the greatest ease and regularity and can be highly recommended. At some of the largest works, from not being acquainted with the *right* way of making the apparatus, they have abandoned automatic regulation altogether, and leave it to the workmen to set the running-off tap of the acid-tanks according to the level of the acid—a very rude method, which, according to the explanation just given, there is no reason for retaining.

Fig. 262.



(Whenever "lead-covered" iron rods are mentioned, it should be understood that for this purpose the iron rod is put into a pressed lead tube of convenient bore, and both ends of the latter are soldered up.)

Some works employ for regulating the rate of feeding the contrivance shown in fig. 262, which is interposed between tap *a* and the central vessel A in the apparatus, fig. 258. The liquid runs from *a* into a leaden box, divided into two compartments, D and E. D communicates with E by the four pipes *f*, *g*, *h*, *i*, placed at different levels, and the lip *k*; E is at the bottom provided with a wide outlet-tube *l*. According to the width to which tap *a* is opened, box D will be more or less filled; with the strongest feed the acid will run into compartment E out of all four pipes and the lip *k*; with a smaller feed fewer of the pipes will come into action. Supposing the attendant to be instructed to work with three pipes, he will have to see that the acid runs out only of *f*, *g*, and *h*, the pressure being almost constant at the level of *h*. This, of course, is greatly preferable to regulating the position of tap *a* by mere rule of thumb, and it operates independently of the level of acid in the main reservoir to which tap *a* belongs. This contrivance acts very well.

Fig. 263.

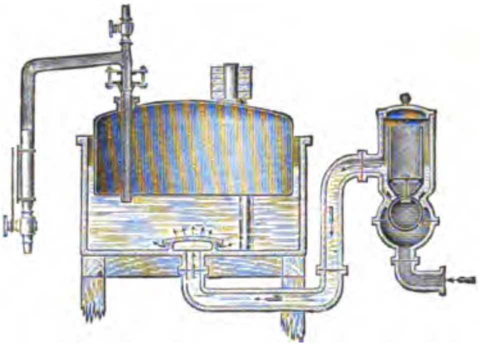


Fig. 264.

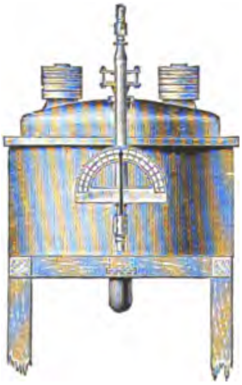
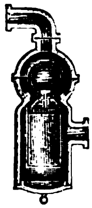


Fig. 265.



Wild's apparatus called "Semper idem" (made by the Vereinigte Thonwaarenwerke, Charlottenburg) realizes a completely uniform velocity of outflow by means of a siphon floating in the liquid, so that the difference of level between both arms of the siphon remains always the same. The outer arm carries an index fixed to the plug of the tap, by means of which the speed of outflow can be made to vary at will. The first rough regulation is produced by a ball-valve. All this is made clear by figs. 263 to 265.

Where the *pulsometers*, to be described below, are introduced, probably one of these is provided for each kind of acid: Glover tower acid, Gay-Lussac acid, chamber-acid. In this case no special regulator for the pressure of outflow is required if the air-cock of the pulsometer is only opened to such an extent that the apparatus can work day and night without pumping up too much acid. The acid-tanks on the top of the towers are once for all filled up to a proper height and are kept at this by the play of the pulsometer with unimportant change of level.

Centralized working of the Gay-Lussac towers.—The following very perfect system is followed at the Griesheim works. Seven sets of chambers are employed, each possessing ordinary Gay-Lussac towers; the whole of these communicate with a large common tower, of a horizontal section of 10 × 30 ft., which receives the fresh acid of 142° Tw., divided into 480 jets. The resistance in this tower amounts to $\frac{1}{12}$ up to $\frac{1}{8}$ in. of water. The weak nitrous vitriol formed here is pumped up and feeds the ordinary Gay-Lussac towers. Since these require variable quantities of acid, this is divided among the seven towers by an acid-wheel having seven chambers of variable dimensions, formed by slightly inclined movable spouts resting on the partitions between the chambers. By shifting these spouts backwards or forwards, the time of feed and also the quantity of acid serving each compartment can be varied at will. From each compartment a pipe conducts the acid to one of the Gay-Lussac towers, where it is again subdivided in the ordinary way. (In the same works there is a similar arrangement for dividing the strong nitrous acid, chamber-acid, and nitric acid among the seven Glover towers, placed at a considerable distance from the central office.) Figs. 266 to 269 illustrate the above. Fig. 266 shows the acid-wheel, supported by the glass bulb α, floating in a vessel filled with sulphuric acid. This avoids all friction, so that the wheel never stops. The glass point β and a short piece of tubing at the bottom form one of the guides; a thimble δ, just

Fig. 266.

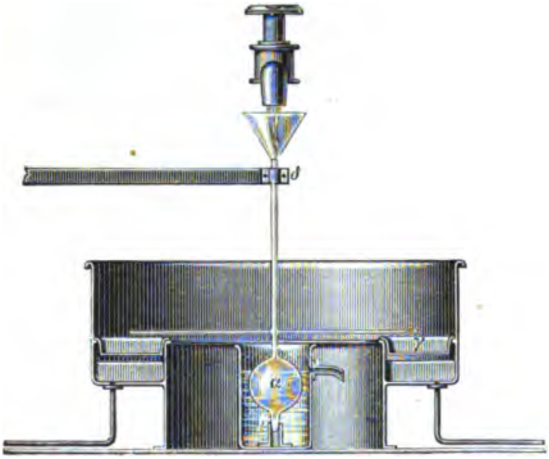


Fig. 267.

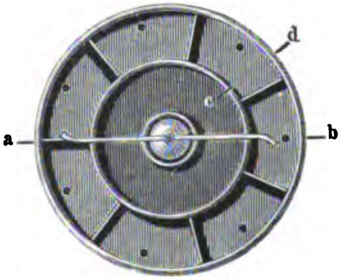


Fig. 268.

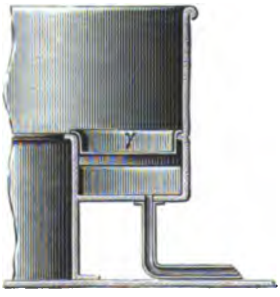
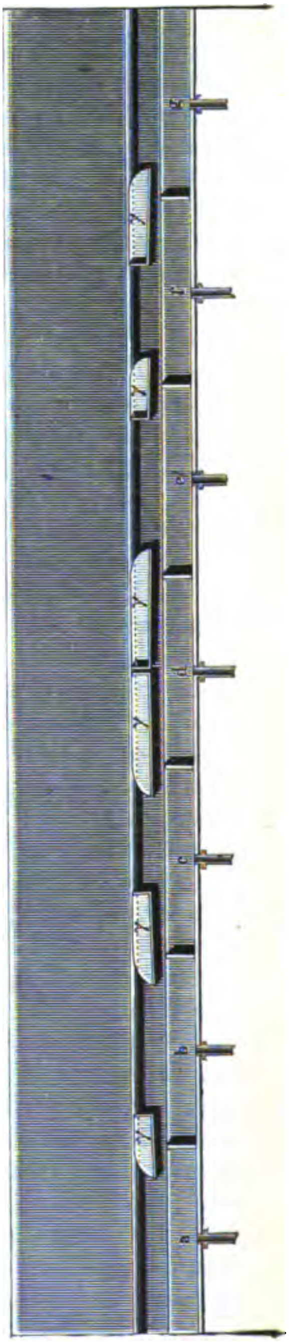


Fig. 269.



below the funnel, constitutes the other guide. We notice the seven compartments *a, b, c, d, e, f, g,* and the spouts γ (fig. 269), which can be moved backwards and forwards, and thus admit of dividing the supply at will. Thus, for instance, in fig. 269, which represents a section through all the seven compartments (projected on a straight line), we find that the acid is divided among the six compartments *a, b, c, e, f, g* in the proportion 7, 7, 7, 8, 5, 8; *d* receives nothing, because the set of chambers to which it belongs is standing still.

At Griesheim the nitrous vitriol is thus brought up to a strength equal to 60 grams $NaNO_3$ per litre, and the total consumption of nitre has been brought down to 0·83 per 100 H_2SO_4. This system allows of keeping one of the sets with an excess of SO_2 (which is very good for concentration in platinum), since the exit-gases from this system are neutralized by the gases of the other sets in the central tower.

Pumping-apparatus for Acid.

It is rarely possible to feed the acid-tank on the top of the absorbing-tower with concentrated vitriol by natural fall; where the concentration takes place in the Glover tower, that possibility is excluded from the outset. There is therefore need for an *apparatus to force the acid up to the top of the absorbing-tower*; the same apparatus will also serve for forcing the nitrous vitriol and the chamber-acid to the top of the denitrating-tower. Ordinary force-pumps cannot be employed here, because these cannot be made without using metals which are acted upon by the acids, at least not for such quantities as have to be treated in this case. Fortunately we have two metals which resist the vitriol very well, viz. cast iron and lead, and with the aid of these an apparatus can be constructed in which the force-pump acts only indirectly, viz. through the compression of a column of air, which thus enters into the forcing-apparatus proper and conveys the acid to any desired height.

The ordinary plan of working (introduced about 1838 by Harrison Blair, according to Richardson and Watts's 'Chemical Technology,' vol. i. pt. v. p. 217) is this, to convey air compressed by an air-pump or, more properly speaking, by a small blowing-engine into the pressure-apparatus, above the surface of the acid, exactly similar to the way in which every chemist in his wash-bottle forces the liquid up in the outlet-tube by blowing air in through another tube. In this there is no special limit of height, so long as the apparatus is made strong enough to resist the pressure and the air-pump is sufficiently powerful.

The air-pumps are generally constructed in this way:—The steam-cylinder and the air-cylinder are both fixed on a common horizontal ground-plate, or cast in one piece with the same; they are then worked by a common piston-rod with a piston at each end. A cross-head sliding between motion-bars gives the necessary guidance; and a pretty heavy fly-wheel secures regular action. The dimensions of the pump are chosen according to the size of the works; for a set of chambers of from 140,000 to 200,000 cubic feet a steam-cylinder of 8 inches diameter, an air-cylinder of 12 inches diameter, and a stroke of 18 inches, with from 40 to 60 revolutions per minute, suffice for pumping all the nitrous vitriol, concentrated acid, and chamber-acid. The compressed-air pipe in this case has 1¼ to 1½ inch bore. Much care has to be taken of the valves of these pumps: if they work with too much noise, they last only a very short time; but, in any case, a second pair must always be ready for putting on when the first give way. At the works formerly managed by myself, I sent the exhaust-steam of the engine into the steam-pipe for the chambers, the steam-boiler belonging to which worked at only 10 lb. pressure per square inch; thus the steam for pumping the acid was got for next to nothing, since only the difference of pressure before and behind the steam-cylinder had to be made good by consumption of fuel. [Comp. p. 531. This description was given in the first edition of this work (1879), and is therefore much prior to the very similar proposal of Sprengel, B. P. No. 10,798, of 1886.]

The air-pipe, which must be made of very strong lead tubing, is not conducted direct from the air-pump to the pressure-apparatus, because in that case acid would inevitably be squirted back into the air-cylinder and soon ruin the valves; but the air-pipe is carried upwards a distance of from 10 to 13 feet, and then as much downwards, before entering the acid-vessel. Close to the air-cylinder a small branch-tube with a cock is soldered on, in order to let out the air when the pumping is finished. Sometimes there is also a pressure-gauge fixed to it: but this is not of much use; for, in the first place, it is soon destroyed by the violent oscillations at every stroke of the piston and by the acid fumes;

and, secondly, the workman can judge much more conveniently than by looking at the gauge, from the noise of the pump and the valves, whether it works easily or heavy—that is to say, with much or little pressure.

The acid-vessel serving as pressure-apparatus is made in various forms. Originally (and even now in many places) it was made in the shape of a soda-water bottle, as shown in fig. 270, afterwards as a horizontal cylinder (fig. 271) with bolted-on covers; but it is now more usually, as shown in fig. 272, a horizontal cylinder with one semicircular and one neck-shaped end, the latter closed by a man-hole door. These vessels are called "acid-eggs." The vessels like figs. 270 are usually lined with lead; those like fig. 271 and 272 are not. Experience has everywhere shown that it is needless to protect the cast iron of the acid-egg by a lining of lead; even the nitrous vitriol and the chamber-acid act so little on cast iron that such a protection becomes unnecessary *. I have found an acid-egg after five years' continuous use for all three kinds of acid

Fig. 270.

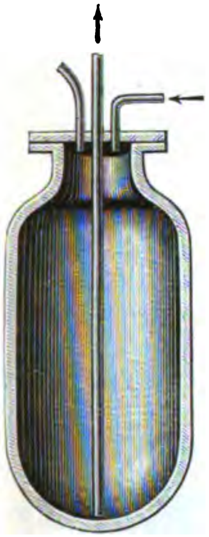
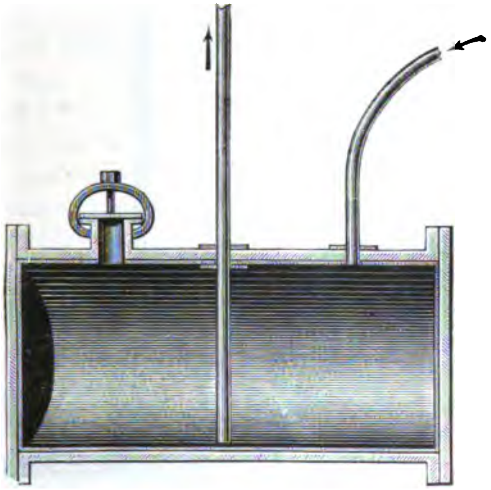


Fig. 271.



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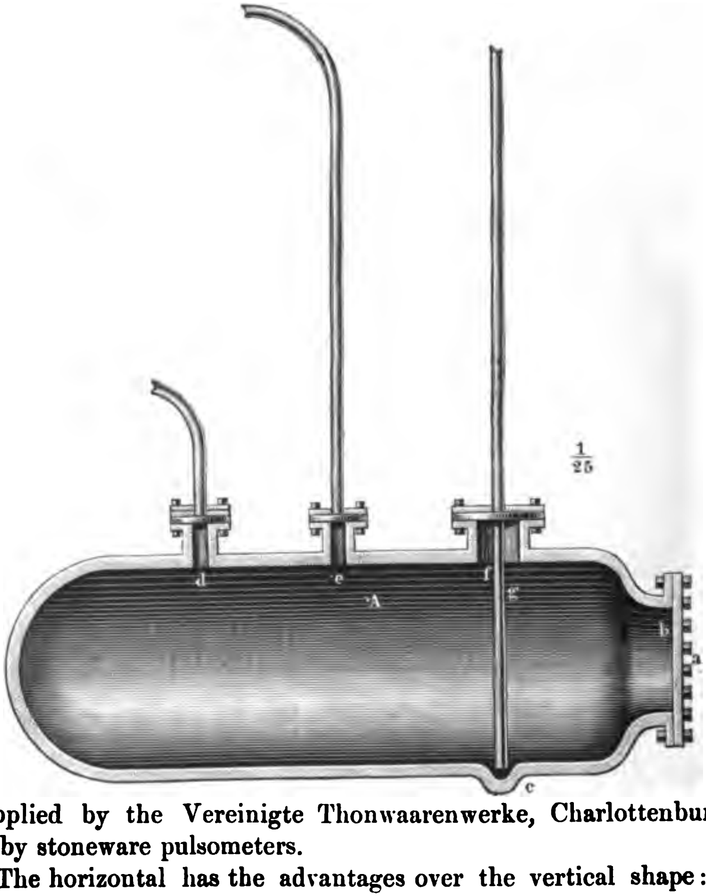
* It has been noticed that the acid-eggs made by some foundries are liable to crack after a few months' use, while those supplied by other foundries, and made like ordinary metal castings, last much longer.

in entirely good working-order. Lining with lead has this drawback, that as soon as a little air gets between the lead and the cast iron through the smallest possible chink the lead is driven away from the iron in many places, and its protecting action becomes quite illusory, whilst the contents of the egg are diminished. ***Dilute*** acids are best pumped up by means of stoneware acid-eggs, as supplied by the Vereinigte Thonwaarenwerke, Charlottenburg, or by stoneware pulsometers.

Fig. 272.



The horizontal has the advantages over the vertical shape:—first, that no well is needed for the acid-egg, which may lie on the floor and thus be accessible all round; secondly, that in the case of excessive pressure, the weakest part (viz. the man-hole) being situated sideways, the acid squirting out is not so likely to injure men and machinery as in the case of squirting out vertically, especially if the cylinder is at once laid with the man-hole turned away from the machinery.

In fig. 272, A is the acid-egg, whose walls are 2 inches thick; *b* is the neck, with the man-hole lid *a* fixed to it by bolts and nuts *; a thick india-rubber washer makes the joint tight; *c* is a recess at the bottom of A, into which the delivery-pipe *g* projects, in order to expel the contents of A as completely as possible; *d*, *e*, and *f* are three branch-pipes—*d* for introducing the acid, *e* for the air-pipe, and *f* (the widest of them) for the delivery-pipe. The pipes have each a strong lead flange soldered to it, which rest on the flanges of the branches *d*, *e*, *f*; by putting loose iron washers on the top, and screwing all three together by bolts and nuts, the joint becomes perfectly tight. The inlet branch *d* may be left open and closed after each filling by a small plate bolted on; but in most cases there is an *inlet valve* for the acid, of the shape shown in fig. 273. (The plain stoppers with lever-rods, figured in Muspratt's 'Chemistry,' cannot support any great pressure.) A and B are acid-tanks, which need not be placed so close to the pressure-valve C as they are represented in the diagram. C is a cylinder of strong lead, about 10 inches wide, whose top is on a level with the top of the tanks, but which is deeper than these, so that they may communicate with C through the pipes *a* and *b*, connected with their bottoms. *a* and *b* end in the bottoms of the tanks with valve-seats of "regulus" metal, and are usually closed by taper valves with long lead-covered handles: no pressure upon these is exercised from below, and therefore they need not be provided with any special contrivance against this. When it is necessary to run the contents of these two tanks, or that of a third tank, not visible in the diagram, but similarly communicating with C, into the acid-egg, the respective bottom-stopper is taken out, the bottom-valve *c* in C also remaining open. The latter valve, which must be very well ground into its regulus seat, communicates through the pipe *d* with the corresponding inlet branch of the acid-egg. On the top it is connected with the lead-covered iron rod *e*, which ends above in a screw-worm e_1, and can be turned by means of the hand-wheel *f*. A very strong iron frame, *g g*, with a female thread corresponding to the worm e_1, is bolted to the bottom-joists, *i i*; both the timber and the iron rods must be very strong, as there is a good deal of strain upon them in screwing the valve in and out. As the cylinder C is equal in height to A and B, it can never run over; and when the acid in C stands at the same level as that in the tanks, the valve *c* is screwed down tight by means of the hand-wheel, the corresponding stopper is put into its seat in the tanks, and the air-pump is started. The whole pressure of the acid, which has sometimes to be lifted to a height of 100 feet, will then act from below on the valve *c*; and unless the latter has been screwed down perfectly tight, the acid will squirt out violently. Although, with a little care on the part of the workman, this should never happen, yet several accidents caused by men being splashed with acid have led to providing the cylinder with a cover and a stuffing-box, *k*, through which the rod *e* passes;

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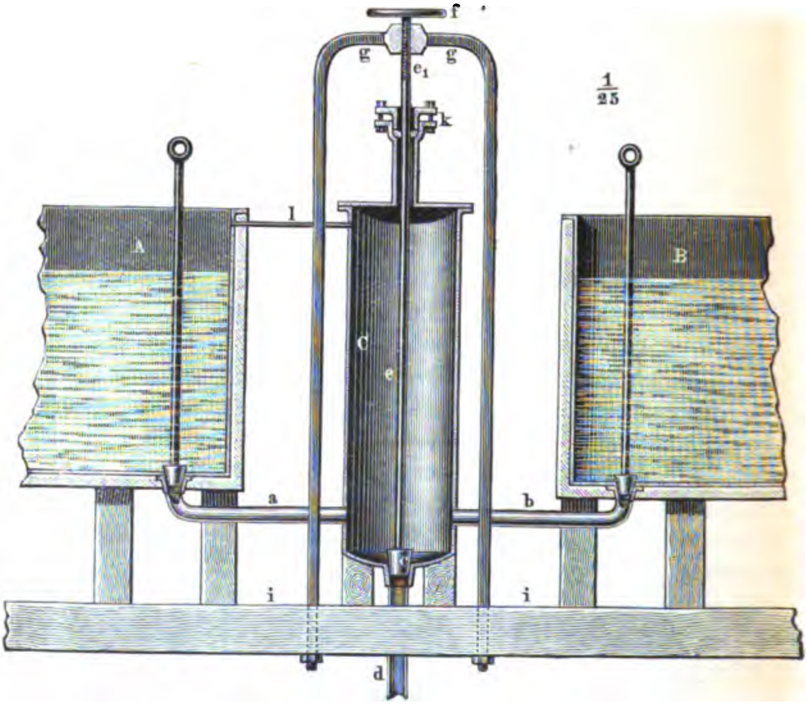
* Some manufacturers propose to construct the acid-eggs without man-holes, as these may render it difficult to keep the joints tight, but the metal-casting must be much more difficult to make.

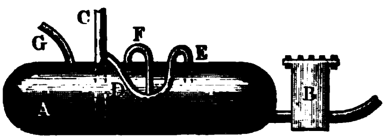
Fig. 273.



the splashing then does no harm, as the acid cannot get out. At the same time the stuffing-box serves as a guide for the valve-rod, which would otherwise have to be provided in some other way. Sometimes (not always) there is a small pipe provided for taking any acid squirted out into one of the three tanks. In this way the same acid-egg can serve for pumping strong acid, nitrous vitriol, and chamber-acid out of their respective tanks one after another.

A self-acting apparatus for filling the acid-eggs, constructed by Mr. Harrison Blair, which, Mr. Mactear says (Journ. Soc. Arts, 1878, p. 558), works well, is shown here according to the description in Richardson and Watts's 'Chemical Technology,' vol. i. part v. p. 217. A (fig. 274) is a strong cylinder of lead closed at both ends [probably cast iron would be preferable]; B a valve-box, and C a delivery-pipe, into which the pipe D enters a little above the vessel. D is continued to E, where it passes to the inside of the vessel, and F joins D at the lowest part. G is the pipe which brings the air from the pump. So long as D contains no liquid, the air from the vessel will pass through, and by thus preventing any pressure on the liquid in the vessel, it will be filled through the valve-box. When the vessel is full, the egress of the air through F being stopped by the liquid, the latter will be forced up E (being lower than F), which, acting as a siphon, fills D and effectually stops the passage of air. As the pressure of air increases, the liquid rises up the delivery-pipe and is conveyed to any required point, while the liquid in D falls with the level of that in the vessel, until this sinks below the bend in D, when the air rushes through, carrying with it all the liquid out of D. This leaves a free passage for the escape of air during the time the vessel is again being filled, the air-pump working the whole time.

Fig. 274.

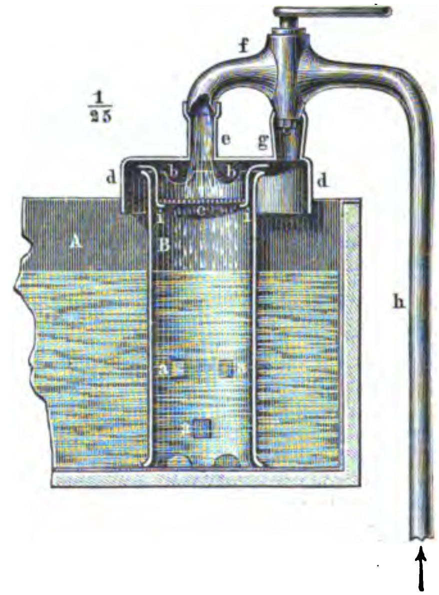


At the Rhenania works the rod *e* of the inlet-valve *c* (fig. 273) is coupled with the air-cock on the acid-egg in such a way that when the egg is full the attendant cannot by mistake shut the air-cock first, but is obliged to screw down the valve *c* before he can shut the air-cock and open the connection with the air-pump.

An automatic acid-egg air-valve is described in Chem. Tr. Journ. xvii. p. 82 (J. Soc. Chem. Ind. 1895, p. 749). The acid entering the egg tends to raise a wooden float, and this lifts a valve connected with the air-tap. When later on the compressed air forces the acid out, the float descends and the air-supply is automatically shut just as the last acid is being driven out.

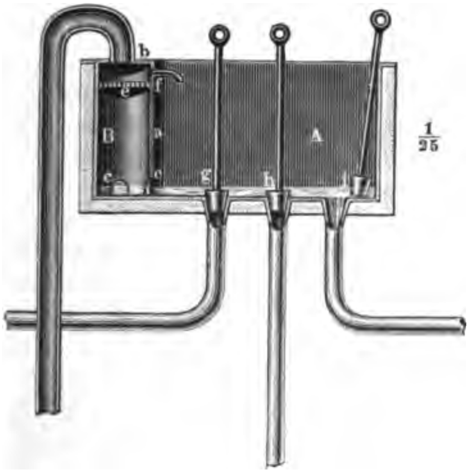
As soon as, in the ordinary kind of apparatus, the pumping is finished, the air-pump, to which now no resistance is offered, begins all at once to go extremely fast, and by its noise draws the attention of the workman to the necessity of stopping it. Directly after, the air-cock in the pipe conducting the compressed air to the acid-egg is opened. Nevertheless some compressed air accompanies the last portions of the acid and rushes vehemently out of the top of the delivery-pipe; and in order to *prevent the acid from splashing about* a special contrivance must be adopted, for instance that shown in fig. 275. A leaden cylinder, open at top and bottom, stands within the tank A; it is jagged out at the bottom in a few places; and the holes *a a* higher up also help to give free communication between B and A. Also the top of B is cut out pretty deeply in a few places (*b b*). Within B the perforated plate *c* is suspended by a few lead strips, *i i*; the whole is

Fig. 275.



covered by a loose cover *d d*, which is kept at a little distance from the top of B by the lead strips, so that the air can escape between them. *d* has a flange of 8 in. depth; in the centre it carries a short tube *e*, to which the "regulus" cock of the delivery-pipe *h* is burnt. Since it is extremely difficult to keep such a cock tight, especially under great pressure, it is surrounded below by the pipe *g*, which also fits into *d*, and thus carries away the droppings. This contrivance acts in the following way:—When the acid forced up through *h* arrives at the top, it runs through *f* and *e*, then through the sieve *c* and into the cylinder B, whence it easily passes through into A. But in the last stage, when compressed air arrives at the same time with the acid, the latter cannot be squirted about, nor can the current of air act upon the surface of the acid within the tank so as to splash it about; for it is broken by the sieve *c* and escapes through the openings of *c* and the annular space below *d* without doing any damage; the acid accompanying it runs quickly down through the sieve *c*. The cock *f* and the pipe *g* are required only when a single acid-egg has to feed several tanks placed at a considerable distance apart, for instance one on the absorbing-tower and two on the Glover tower; for then the delivery-pipe must be divided into two parts, and each must be provided with a stop-cock, only that leading to the working tank being open. If, however, the tanks to be filled are placed

Fig. 276.



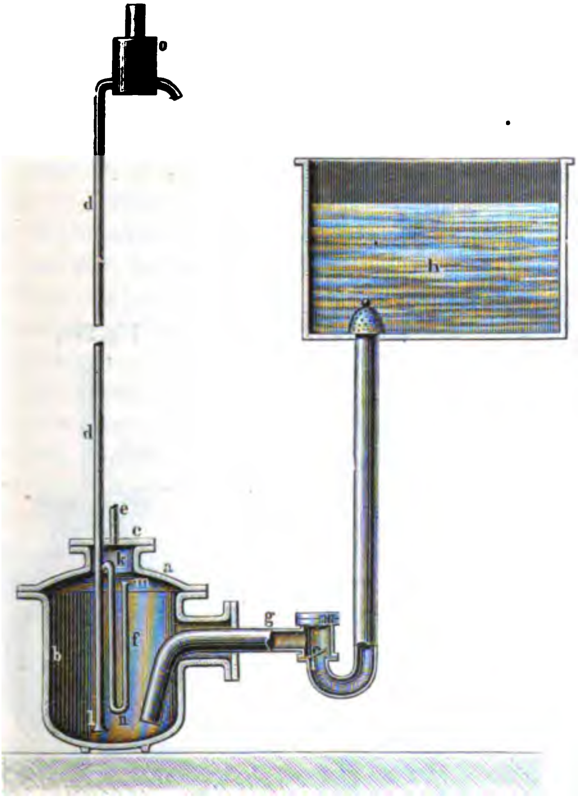
close together, no cocks are required, but the simpler arrangement, fig. 276, can be employed, which may also be made much smaller than (for the sake of clearness) it has been drawn here. Within the same lead-lined box A there is a special compartment B constructed by means of a lead partition, *a*, and cover, *b*. The side of B is jagged out at the bottom at *c c*, in order to communicate with A. The delivery-pipe fits into the cover *b*; the air rushes against the sieve *e* and escapes out of the pipe *f* without doing any harm. In the bottom of A there are three valve-seats, *g*, *h*, and *i*, connected with as many pipes leading to different tanks; but only one of the valves is left open at a time; the two others are closed by plugs, and the tanks communicating with them therefore receive nothing.

In smaller works there is usually only one acid-egg, which serves for pumping all the strong acid, nitrous vitriol, and chamber-acid, one after the other. In this case the air-pump has nothing to do during the time that the egg is getting filled from one of the tanks; but if the cubic contents of the chambers do not exceed 200,000 cub. feet, there is time enough for that. But where the chamber-space is larger, two acid-eggs, at least, will be required, of which one usually serves for the strong acid and nitrous vitriol, the other for the chamber-acid; in this case the same air-pump can do all the work if the air-delivery pipe is provided with two branches and two stop-cocks, one of the eggs always getting filled whilst the contents of the other egg are being pumped up; the air-pump is thus fully utilized.

Johnson and Hutchinson (E. P. 8141, of 1885) describe a combination of three upright vessels, so connected that the compressed air contained in one is always utilized in the next, and is not lost as in the usual process.

A somewhat different kind of acid-lifting apparatus is Laurent's pulsometer. It is made of cast iron for sulphuric acid with lead pipes (figs. 277 and 278), and of stoneware for hydrochloric or nitric acid (fig. 279). In the former case the joint between the cover *a* and pan *b* is best made good by a lead washer, in the latter case by an india-rubber washer; *c* is the man-hole, with the rising-main *d* and the pipe *e* for compressed air. The rising-main *d* has a side connection with the swan-neck pipe *f*. The feed-pipe *g* is connected with the store-tank *h*; the latter must be fixed at such a height that even when the pulsometer is quite full, and *h* nearly empty, there is still a greater head of liquid on the pulsometer then the length of pipe *f*. The clack *i* (which may be replaced by a ball-valve or by a Bunsen valve, as shown in fig. 279) prevents the acid from being driven back into *h* whilst rising in *d*. Pipe *d* must be fixed in such a manner that it can be taken out together with pipe *f*, in order to attend to the latter.

Fig. 277.



The play of the apparatus is as follows:—The acid runs from *h* through *g* into *b*, during which time the air, continuously being forced in through *e* from the air-pump, escapes through *f* and *d*. As soon as vessel *b* has been filled to the upper opening of *f*, the air cannot escape very well, and a little pressure ensues. In spite of this, through the momentum of inertia, the acid rises still a little, arrives at the top of the siphon (at *k*), and causes this to act, whereupon the level of the liquid in all the pipes becomes that of the outlet of *f*, that is *m*. As the air cannot now escape, the

Fig. 278.

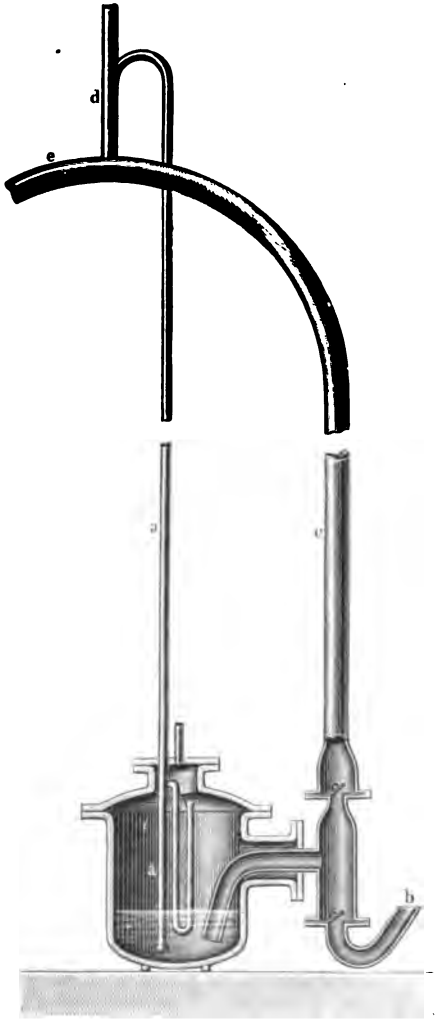
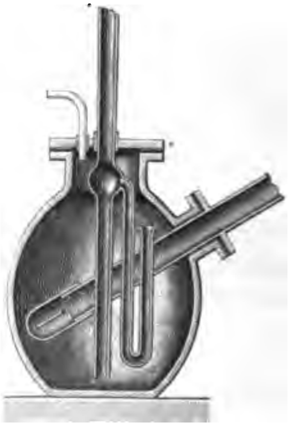


Fig. 279.



pressure gradually gets up and the liquid rises in pipe *d*, but sinks in vessel *b*. As the pressure on the surface of liquid in *b* must be the same at all points, and each point has also to bear the counter pressure of the column of liquid in *d*, the acid must sink exactly as much in the outer limb of *f* as in the vessel *b*, and the level must at last arrive at *n*. Now as the column of liquid between the lower end *l* of pipe *d* and the upper outflow at *o* is still rather higher than that from the lowest point *n* of the siphon to the outflow at *o*, the air must throw the acid from *n* out of *o*, the pressure within *b* must cease, and the vessel *b* must be filled again from *h* through *i* and *g*. Even if a little acid had accidentally run back from *d* into *f* and filled the siphon, this would not prevent the filling of *b* from *h*, since this tank (as we have seen above) is placed high enough for this purpose.

If during the forcing up of the acid the outflow from *o*, owing to the friction in *d*, were not so great as corresponds to the volume of air entering at *b*, strong pressure will ensue on the surface of the liquid in *b*, and at last the acid in siphon *f* would be forced to point *n* before the outer level in *b* had sunk to that point. Then the air will bubble up through *n* into *d* and out of *o*, and will keep the liquid column suspended. This bubbling can be perceived when the ear is put close to *d*, and can be remedied by closing the air-pump cock a little, and afterwards regulating the pressure in the following way:—In the air-pipe *e*, which is $\frac{1}{4}$ of an inch wide, a flanged joint is made between the cock (not shown here) and the cover *c*, in which a copper disk is placed, perforated with a pin-hole (say $\frac{1}{24}$ inch). If with the cock quite open this hole is still too wide, so that the air, instead of lifting the acid, bubbles through *d*, the pin-hole is narrowed to the required extent so that in future the tap may be opened fully whenever the apparatus is to act. It can then go on for many years without any supervision, unless the valve *i* gets obstructed by impurities.

As, during the time *b* is getting filled, the air escapes without being utilized, it is best to place the tank *h* at least five feet above *b*, and make pipe *g* very wide, so as to shorten the time of filling. The compressed air must always be under the same pressure, and the air-pump must therefore have a regulator of some kind. The pin-hole in the regulating-disk must be arranged for the highest pressure which may be expected.

It is possible to lift liquids to a greater height than corresponds to the pressure of air present, by placing a second pulsometer midway up the height to be overcome, and regulating both pulsometers so as to act together. Above all, valve *i* must be kept in order; for strong sulphuric acid it must be made of lead (regulus metal) and very carefully; for chamber-acid or hydrochloric acid it may be made of india-rubber.

This apparatus, once properly set, acts day and night without any supervision; it is started or stopped in a moment by opening a tap.

Fig. 277 shows a pulsometer of 50 litres total, and 40 litres available space; the rising-main must be 1⅜ inch wide; in the case of a wider pipe part of the acid would run back and air would rise up. The apparatus can act 30 times per hour, and lift 25 to 30 cubic metres (say 875 to 1050 cubic feet) per 24 hours. Fig. 278 shows an apparatus intended for greater speed; there is a rising-pipe *a* of 1 to 1⅜ inch width, provided with a valve, and a much wider feed-pipe *c*, also provided with a valve. The latter must always be full; the outflow thus takes place under the pressure of the liquid column *d e*, and therefore very quickly. Fig. 279 shows the form best adapted for stoneware vessels, which should stand a pressure of 4 atmospheres.

Simon (Zeitschr. für angew. Chem. 1890, p. 356) describes a combination of two similar pulsometers which utilizes the compressed air otherwise escaping during the filling of the vessel, the apparatus being connected by a Y-pipe and automatic ball-valve.

The principle of the pulsometer has been improved by replacing the siphon by a float-valve and most thoroughly worked out by Paul Kestner, of Lille. His pulsometers are illustrated and described in our vol. ii. 2nd ed. p. 408 *et seq.*; in the present volume we have also shown on p. 146 a Kestner's pulsometer as constructed for nitric acid. Most chemical works now employ these apparatus, and speak very highly of them; many works have abolished the acid-eggs entirely in favour of Kestner's pulsometers.

At Freiberg, in 1902, Kestner pulsometers (which are still doing very good work) were in use, as well as real pumps. One kind of these is made of antimonial lead ("regulus metal") with valves of phosphorus-bronze, another consists of a cast-iron barrel, lined inside with lead, with a porcelain ram and phosphorus-bronze valves. The former serves only for pumping up to 33 feet, the latter up to 80 feet (25 metres) by means of a 10-inch conduit. Both these and the Kestner pulsometer, which is used for the Gay-Lussac and precipitating towers, give entire satisfaction.

C. Simon, of Stolberg, has constructed a pneumatic acid-pump, provided with an automatically acting piston governor, which is stated to be superior to the regulation by floats in various respects. Comp. also Plath, on mechanical means for raising acids, Zsch. f. angew. Ch. 1902, p. 1211.

We shall here refer to the construction of *tanks or reservoirs* for sulphuric acid (much of which will apply also to hydrochloric and nitric acid). *Open* reservoirs for sulphuric acid are always made of lead, usually in the way shown in fig. 276 and elsewhere, viz. a strong wooden frame to which the lead sides are fixed by means of straps, turning the upper edge over the top, just as in the construction of chambers, or else a box made entirely of wood with lead lining; in each case the thickness of the lead need not exceed 5 or 6 lbs. per superficial foot, if the wood frame is so constructed as to take all the side thrust; but it is preferable to use thicker lead, say, 9 or 10 lbs., on account of wear and tear. Where it is intended that the acid run into the tank in a hot state should cool therein, the tanks are much better made circular in shape, of much thicker lead (say 10 lbs. or more), and strengthened on the outside with strong iron hoops, which may be connected by strong cross-stays in the case of very large tanks. Considering the increase of pressure from the top downwards, the binding-hoops should be placed nearer together in the lower part of the tank.

Even *brickwork* may serve for acid-tanks (sulphuric, hydrochloric, nitric acid), if the bricks, tiles, stones, &c. are acid-proof. Volvic lava is the best material (comp. later on). The mortar in this case should be that described on p. 120; viz. a paste made of asbestos powder and silicate-of-soda solution, with or without some other solid admixture, as barytes &c. This mortar should at first not be brought into contact with water, which would dissolve out the sodium silicate, but at once with acid, which causes silicic acid to be separated in the solid state and to render the joints perfectly tight.

For *closed tanks* for sulphuric and strong nitric acid the best material is *iron*, either cast or wrought iron, as may be most suitable for constructive purposes; and this material is also adapted even for *pipes* &c., in cases where no air can enter, whose moisture might dilute the acid.

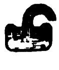
Working the Gay-Lussac Tower.

After the above explanations very little need be said as to the working of the absorbing-tower. The following points have to be observed in this respect.

The *gas* entering the tower must show a distinctly red colour in the "sight;" on the other hand, the exit "sight," behind which a board painted white ought to be placed, should show a perfectly colourless gas. The gas escaping from the top of the tower, or of the chimney connected with it, ought not to produce any considerable amount of red vapours when it meets the outer air (see below). Furthermore the chamber-gas before entering the tower should be as *dry* and as *cool* as possible, lest the absorbing-acid be diluted or heated. For this purpose the last chamber receives very little, sometimes even no steam, so that its acid remains at about 106° Tw.; moreover the gas is often conducted through a long pipe or a tunnel, or into a shallow box with several vertical partitions, where it has to move backwards and forwards. In these cooling-apparatus water may be applied outwardly to assist the cooling, especially in summer-time. Sometimes the bottom of the box is covered with strong vitriol, in order to dry the gas; this, however, to a certain extent, only anticipates the tower. The *sulphuric acid* serving for absorption must show at least 144° Tw.; but this is only a minimum, which ought to be exceeded if possible; acid of 148° absorbs much better, that of 150° or 152° Tw. better still; wherever possible, acid of 152° Tw. should be taken for the absorption. Such acid can be got without any difficulty from the Glover tower—with more difficulty from pans placed on the top of the pyrites-burners, where the acid rarely gets beyond 144°. Schwarzenberg even proposed to use acid of 170° Tw., because it absorbs three times as much as that of 144°; but this is out of the question, owing to the large additional cost of concentrating from 152° to 170°.

Above every thing care must be taken that the acid used for absorbing is as *cool* as possible. Hot acid absorbs very badly; much nitre is lost; and at the same time a weak nitrous vitriol is produced. Bornträger (Dingl. Journ. vol. cclviii. p. 230) goes so far as to suggest cooling the acid down to 5° C., but it is hardly possible to go to that length. In fact, at the French works they believe that 25° is the best working temperature. It is therefore necessary either to provide a very large tank for cooling the vitriol concentrated in pans or in the Glover tower before it is used in the Gay-Lussac tower, or else (as the cooling by mere exposure to the air is a very slow process, especially in summer, and in large works enormous tanks would be required for it) special cooling-apparatus is employed. As such many works use double spouts—an outer one filled with water, and an inner one, in which the hot acid runs. In this case it is rarely possible to apply the rational principle of running the cooling-water in a current opposite to that of the acid to be cooled, because, on account of the length of the spouts, there is no fall for this. Such double spouts also have a disagreeable tendency to swell out at the bottom whenever a little more pressure takes place, because the lead when hot diminishes in strength, which in any case is not considerable. This drawback can be avoided by the arrangement sketched in fig. 280, viz. by attaching to the spout, at about every 30 feet of its length, a tube rising perpendicularly from the double bottom through the upper spout and bending over the side of the latter; the water can issue out of this, in case of stronger pressure, without mixing with the acid. The upright tube also serves for the escape of the air-bubbles which are often contained in the water, and which may stop the stream as well as cause the spout to bulge out.

Fig. 280.



On pp. 551 to 553 of our second edition a tubular cooling-apparatus is described and illustrated, to which we merely refer here as it is now obsolete.

A simpler but perfectly efficient cooling-apparatus is found in most German works. The acid runs out of the Glover tower immediately into a cylindrical trough of thick lead, about 2 feet high and wide, and runs out of it again through a pipe coming away sideways from its bottom and turned upwards. In the trough there is a narrowly wound lead coil or even two such coils, through which cold water is continually running from above; getting heated in the bottom part of the coil, it rises up and is taken away hot at the top. The cooling here generally goes down to 40° C., and is supplemented by letting the acid stand in tanks ; but 30°–35° C. might easily be attained. This is a very rational method of cooling, because the hot acid running in at the top comes into contact with the upper, hot part of the water-coil, whilst the acid ultimately flowing away from the bottom, which is already cooled down to a great extent, is cooled still further by the cold water in the bottom of the coil. There is also no trouble caused by any deposit forming in the acid, if there is a sludge-valve provided in the bottom of the trough.

At some works I have seen a good cooler which I describe from notes supplied to me by Dr. Stahl. A flat pan, say 30 ft. long, 5 ft. wide, and 6 in. deep, made of wood and lined with 6 lb. lead, is divided lengthways into ten narrow channels by leaden strips, 4 inches wide and 6 inches apart. Each strip stops alternately 6 inches from the ends of the pan, so that a zigzag channel is formed, into which a 1-inch or 1¼-inch lead pipe is laid, forming a coil of 200 feet in length. The acid runs through the zigzag trough, and cold water in the opposite direction through the lead pipe. Where the hot acid enters, a double loose lining, made of 4 ft. length of heavy 2-inch pipe, cut open lengthways, is put into the trough in order to protect it; this piece must be renewed about once every six months, and if this be observed the trough will not require any repairs for many years. A cooler of the above-stated dimensions suffices for cooling 18 tons of hot Glover-tower acid down to about 30° C. every 24 hours.

Crowder (J. Soc. Chem. Ind. 1891, p. 300) describes a cooling-arrangement practically identical with that described here; and he gives details concerning its function. The acid travels altogether about 1000 feet, and its temperature is brought down from 139° or 149° C. to 28° or 39° C. Further on (p. 304) he contends that such cooling is unnecessary (except, perhaps, in order to save the lead from quick corrosion), on the strength of laboratory experiments in which acid of spec. grav. 1·75 did not absorb the nitrous vapours from chamber-gases much less at 100° than at the ordinary temperature. But as he never went beyond 0·47 or at most 0·69 per cent. N_2O_3 in the acid, his statements are not to the point. We know from experiments made on the nitrous-acid tension of sulphuric acid that this increases rapidly with the percentage of N_2O_3, and in all cases with the rise of the temperature. As regards such low percentages of N_2O_3 as those employed by Crowder, the tension of N_2O_3 is not very great even at higher temperatures; but in actual work we must aim at higher percentages of nitre, in which case any higher temperature of the acid would act injuriously. This has been fully confirmed by observations communicated by Hasenclever (Chem. Ind. 1893, p. 337). A high temperature not merely prevents the absorption of N_2O_3, but even expels it from stronger nitrous vitriol.

At large works the two systems of cooling just mentioned are sometimes combined. I consider as perhaps the best plan a perpendicular cooler, similar to that which has been adopted at several coal-tar works for cooling benzene vapours (*comp.* Lunge's 'Coal-Tar and Ammonia,' 3rd edition, fig. 172, p. 591); that is, two short, cylindrical or square boxes, one above the other, connected by a very large number (50 to 100) of narrow, perpendicular pipes, about 2 feet long and ½ inch wide, the whole standing in a wider tank supplied with cooling-water. Hot acid is run into the top box, slowly finds its way downward through the thin pipes, which possess a very large cooling-surface, and arrives cool in the bottom box, whence it rises up in a special pipe and is run off almost on a level with the top box. The bottom box must be provided with a sludge-valve. Or else the acid is contained in the outer tank, and cooling-water is run through the system of boxes and pipes just described.

Very efficient cooling might be produced by the action of a current of air, either by forcing this through the hot acid, or else by running this down a tower in which air rises up by the action of a fan-blast or by chimmey draught; but where very large quantities have to be treated, the supply of cooling-air might require too much power to be economical.

In ordinary circumstances the absorption in the Gay-Lussac tower requires *at least* one half of all the acid produced. This is got from the Glover tower without any other cost but that of pumping up; in the case of other denitrating apparatus the cost of concentration has to be added to this. Frequently the necessary quantity of absorbing-acid is stated at a lower figure—for instance, as one-third of the whole production; but this in most cases is certainly insufficient, and no doubt a large loss of nitre would result from it. On the other hand, manufacturers working with Glover towers, who, apart from the trifling expense of pumping, have no concentrating-expenses at all, send all their acid once a day through the Gay-Lussac tower. This is quite right. Bode ('On the Glover Tower,' p. 49) calculates that with a loss of 4 parts of nitre or 1·75 of N_2O_3 to 100 parts of acid of 170° Tw., the absorption requires at least 56 per cent. of *all* the acid of 144° manufactured, if very strong nitrous vitriol (with 1·75 per cent. of N_2O_3) is to be obtained. Such strong nitrous vitriol, however, is not obtained in ordinary working; and therefore considerably more than 56 per cent. of all the acid manufactured must be run through the Gay-Lussac tower in order not to lose any nitre. In fact, some manufacturers send much more than their daily make through the Gay-Lussac towers; but at some of the best-conducted works they manage with about $\frac{4}{5}$ or $\frac{5}{6}$ of the daily make. Of course, everything depends upon the style of working the chambers. With the ordinary style, where there is about 20 cubic feet of chamber-space to each lb. of sulphur burnt in 24 hours, the above-quoted figures are quite sufficient; but the forced style of work, frequently adopted in France, where there is not much more than half the just-mentioned chamber-space (pp. 463, 561, 581, and below), cannot be kept up except by a very large floating capital of nitre, and in this case twice or more the daily production of acid has to pass through the Gay-Lussac tower. I am, even in England, acquainted with two very large works (belonging to the same firm) in which the quantity of acid run down the Gay-Lussac towers is from three to four times the daily make; and in this case the ordinary chamber-space of 20 cubic feet is allowed. But it seems doubtful whether such an enormous feed of the towers is advantageous (apart from the cost of pumping), considering the action of the coke on nitrous vitriol (pp. 231, 485, 585). At other works I have found $1\frac{1}{4}$ or $1\frac{1}{2}$ times the daily make of acid run through the Gay-Lussac tower, and so forth.

At Griesheim they employ 75 per cent., at Stolberg (1902) about 200 per cent. of the daily make in the Gay-Lussac tower.

Sorel ('Traité,' p. 312) supplied a Gay-Lussac tower at one of the St.-Gobain works with 39,000 litres acid of 60° where the chambers produced 2·75 kils. H_2SO_4 per cubic metre, with 45,000 litres for a production of 3·0 kils., with 52,000 litres for 3·5 kils., and with 62,000 litres for the "high-pressure" production of 4 kils. per cubic metre. In every case the average consumption of nitre was 0·8 kil. for 100 kils. H_2SO_4, or 2·45 kils. for 100 kils. sulphur burned. [This statement differs very much from the figures given by Mr. G. E. Davis (*supra*, p. 469), according to which the consumption of nitre was much greater in the case of high-pressure work, but even as regards the easiest work it was much higher than the consumption attained by Sorel at high-pressure work.]

The specific gravity of the *nitrous vitriol*, as the acid issuing at the foot of the Gay-Lussac tower is called, does not differ very much from that of the acid fed in at the top. In the usual case, where there is ample chamber-space and the sulphuric acid is almost entirely condensed in the last chamber, the mixture still necessarily present in the exit-gases is, of course, absorbed by the stronger acid in the Gay-Lussac tower, and the nitrous vitriol running out at the foot is then 1° or even 2° Tw. weaker than the feeding-acid. But with the "forced style" of working in France there is a considerable quantity of acid contained in the exit-gases in the shape of mist, which is retained in the Gay-Lussac tower, and, added to the nitrososulphuric acid absorbed, may make the nitrous vitriol even a little stronger than the feeding-acid.

When properly treated, nitrous vitriol ought to be very little coloured, and should have only a slight smell of nitrous acid; but on being diluted with water, especially hot water, it ought to effervesce strongly and give off thick red vapours. At a few works this rough test is considered sufficient for judging of the quality of the nitrous vitriol; but at all the better works it is probably tested in the laboratory, which can be accomplished in a very short time by the permanganate method (comp. p. 262). Now and then this should be supplemented by a testing in the nitrometer, in order to make sure that nitric acid is present or not. By these testings it can be seen from day to day whether the percentage of nitre increases or decreases. In the former case, if the other tests of the chamber-process agree with it, this is an intimation that some of the nitre must be taken off; in the latter case this test will, better than any other, show, before any damage has been done, that more nitre is required. In any case nitrous vitriol should not contain less than 1 per cent. of N_2O_3; above 2½ per cent. it is too strong, and there is danger of nitrous gas escaping without being absorbed, which can be controlled by the colour of the exit-"sight." In this case more strong acid must be charged at the top; and if there is an excess of nitre-gas in the chambers, a little less nitre must be used.

The Gay-Lussac acid, or nitrous vitriol, is essentially a solution of nitrososulphuric acid ("chamber-crystals") in sulphuric acid. Formerly it was believed that it regularly contained some nitrogen peroxide or nitric acid (Winkler, Kolb, Hurter, Davis, &c.); but this assertion was only caused by the imperfection of the then employed analytical methods, as shown for Winkler's and Kolb's results by myself (Chem. News, vol. xxxvi. p. 147), the nitric acid being generated during the analyses themselves. The contrary fact, viz. that *ordinary* nitrous vitriol contains no appreciable quantity of nitric acid, was first proved by me; and it has been confirmed by several subsequent investigators. This is even the case when so much nitre has been introduced intentionally, as in Lunge and Naef's experiments, or by inadvertence, that the last chamber contains some nitrogen peroxide (Chem. Ind. 1884, p. 10). It has been shown before (pp. 231, 485, 585) that this is no doubt due to a reduction of the nitric acid, originally formed from the nitrogen peroxide, by the coke packing of the Gay-Lussac towers. With columns filled with a non-reducing packing probably nitrous vitriol containing nitric acid would be much more frequently met with; but with coke-towers, and with the ordinary style of working employed in all English and German and formerly also in all French works, it is one of the signs of the regularity of the process if *no* nitric acid occurs in the nitrous vitriol. Probably it is different with the French "forced style," where the chambers are made to turn out nearly twice as much as before, by supplying them with a comparatively enormous quantity of nitre (without, however, losing more of it in the long run, owing to correspondingly large Gay-Lussac towers). In this case it follows most distinctly, from Lunge and Naef's observations (next Chapter), that there must be a *large* quantity of nitrogen peroxide in the last chamber, too large to be completely reduced by the coke to N_2O_3, so that the nitrous vitriol will be found to contain some nitric acid.

A very strange error has for many years existed, both in all publications on the subject, and in the ideas of nearly all those practically concerned in the manufacture of sulphuric acid who gave any attention to the chemistry of the subject. This error is: that nitrogen peroxide, N_2O_4, forms only a "loose" combination with sulphuric acid of such concentration as is employed for working the Gay-Lussac tower, and that, therefore, very little N_2O_4 is absorbed in that tower, unless it can be there reduced by SO_2 to N_2O_3. This erroneous assumption, coupled with another error, viz. that the "nitre" in the chamber exit-gases consists essentially of N_2O_4, and the *true* observation that the "nitrous vitriol" generated in the Gay-Lussac tower does not contain anything but N_2O_3, has led to the invention of Brivet, Lasne, and Benker (G. P. 17,154), who introduce into the exit-gases, on their way between the last chamber and the Gay-Lussac tower, a certain quantity of burner-gas, by means of a steam-jet. The excess of moisture thus imparted to the burner-gas is removed by means of a small coke-tower fed with Glover-tower acid, and the gas is now mixed with the chamber-gases before entering the Gay-Lussac tower. It was supposed that the nitrogen peroxide would thus be reduced:

$$N_2O_4 + SO_2 + H_2SO_4 = 2\,SO_2\,(OH)\,(ONO).$$

No doubt this would be really the case if an appreciable quantity of "free" N_2O_4 did exist in properly composed exit-gases; but this is not so, at least with the ordinary, not "forced," work. I have, moreover, conclusively proved (Berl. Ber. 1882, p. 488) that there is no foundation for the assumptions underlying the above-mentioned patent, more especially the idea that N_2O_4 did not easily and completely dissolve in sulphuric acid of 142° Tw. In fact the first favourable reports upon the practical success of that patent process have not been confirmed by subsequent observations, and it must be held that for properly-managed chambers the process offers no advantage.

Benker has several times reverted to proposals, founded upon the alleged difficulty of absorbing N_2O_4 in the Gay-Lussac tower, by introducing SO_2 at some place where it is to reduce N_2O_4 to N_2O_3; he has, however, found that this cannot be done in the Gay-Lussac tower itself, and he therefore injects the SO_2 into the last chamber or a special chamber placed between this and the Gay-Lussac tower (G. P. 88,368). The mixture of gases in this case should be very thorough, and it is therefore preferable to employ the SO_2 not as burner-gas, but in the shape of a large quantity of gas from the first chamber, where much SO_2 is still present (G. P. 91,260). This last idea is evidently much the same as the various proposals formerly made for mixing the chamber-gases from various parts of the system (*suprà*, p. 476).

The success of the working of the Gay-Lussac towers depends also upon the proper *regulation of the draught*. If the draught is insufficient, the chamber-process will from the outset be injured by the continual leakage of gas and by all the other drawbacks already enumerated, and especially by the behaviour of the pyrites in burning. In that case the Gay-Lussac tower itself will not work properly; for unless a sufficient excess of oxygen be present in the last chamber before the gas leaves it, unoxidized nitric oxide will remain behind, which will pass through the tower unabsorbed and only form red vapours when issuing into the outer air. At the same time there will be sulphur dioxide present in this case; and this acts still worse, since it decomposes the nitrososulphuric acid still present in the vitriol with which the coke in the tower is soaked, and carries away its nitre as nitric oxide. If the waste gas, as previously insisted upon, contains 5 or 6 per cent. of free oxygen, the above cannot happen to an appreciable extent.

If, on the other hand, the draught is too strong, and therefore the kiln-gas is too poor, the sulphur dioxide will not have time to condense within the chambers as sulphuric acid; it will partly get into the tower, and there cause the decomposition just mentioned and loss of nitrous compounds.

In both cases, therefore, the same result will happen as if the last chamber did not contain an excess of nitre-gas; and if nitre is too much economized, it will indeed be wasted all the more in the way just described, the sulphurous acid driving off the nitrogen of the tower-acid into the air in the shape of nitric oxide.

Such a faulty working of the tower will reveal itself by the escape of too much red vapours out of the chimney, by the tests of the tower-acid, and even by its appearance, since the acid, which otherwise is nearly or quite colourless, turns of a dark purple, and is filled with countless small bubbles of nitric oxide, at the same time getting heated by the formation of sulphuric acid (Bode, in a note to the translation of H. A. Smith's pamphlet, p. 122). It is therefore the worst case of all, if alternately sulphur dioxide gets into the tower and the reverse. In that case nitrous vitriol is alternately produced and again decomposed. When, however, sulphur dioxide constantly passes into the tower, there is no absorption of nitre-gas at all, and the tower in this case does not act as an absorbing-apparatus, but simply as a continuation of the chamber-space (Bode, ib. p. 124). This proves, as Bode justly remarks, that one improvement, viz. the recovery of the nitrous acid, necessarily led to another, viz. to a better condensation of the sulphur dioxide, or a better yield on the sulphur burnt.

The loss of nitre caused by this imperfect action has been often underestimated, especially formerly when the methods for testing the exits were defective; indeed the very reasons which impede the full action of the Gay-Lussac tower will cause similar losses during the bubbling of the exit-gases for the purpose of testing through the absorbing-liquids on the small scale. It is quite certain that the loss of nitre in the exit-gases indicated by Jurisch and others is far below the truth, and that this vitiates by itself most of the reasoning concerning the "chemical loss" in the Glover tower. Benker (quoted by Sorel in his 'Traité,' p. 313) has found that the Gay-Lussac sometimes lets two-thirds of the nitrous gases escape, and Sorel (pp. 313 & 393) agrees with him, on the strength of calculations founded upon the vapour-tension of N_2O_3 in nitrous vitriol. He found this *unavoidable* loss to cover very nearly the whole loss of nitre in his chamber system, viz. 2·66 per cent. out of 2·8 per cent. $NaNO_3$ for 100 S, leaving practically no "chemical loss," seeing that a little nitre escapes with the sulphuric acid withdrawn for use or sale.

The exit-gases issuing from the Gay-Lussac towers, even when these are of very large dimensions, are never free from either sulphur or nitrogen acids, and must be regularly tested to comply with the demands made by law, as will be described later on.

We cannot indeed expect the Gay-Lussac tower to absolutely retain the last traces of acids, especially the nitrous fumes, for the following reasons: that a solution of N_2O_3 or of HSO_5N in sulphuric acid of 140° Tw. possesses already a certain vapour-tension, causing some N_2O_3 to be volatized in a current of air (comp. p. 228); that the contact of the gases with the acid can never be made absolutely perfect; and that the time during which this contact takes place is very short. Sorel (*l. c.* p. 313), calculates it for the best and largest apparatus at two minutes as a maximum.

It is a well-known fact that at the very best-managed acid-works the gas issuing from the Gay-Lussac tower has a slight ruddy or orange colour, most of which is probably caused by NO, which finds too little oxygen within the tower, but turns into NO_2 in contact with air. Most acid-makers regard it, from experience, as a bad sign for the working of the chambers, if the orange vapours entirely cease. The Benker process (p. 626) which has a tendency to increase the quantity of NO must also increase this orange vapour in the exit-gases, which, of course, is best noticed where the gases issue from the Gay-Lussac straight into the air, not into a chimney.

Crowder (J. Soc. Chem. Ind. 1891, p. 303) gives a table of averages of the amount of acids contained in the gases both on entering and on leaving the Gay-Lussac tower. The gases on entering contain from 3 to 4 grains of acid per cubic foot, reckoned as SO_3 (but in reality consisting of SO_2, H_2SO_4 in the shape of mist and nitrogen acids), on leaving only about 1 or 2 grains. He believes that, if the gases contain more than this quantity, it indicates that sulphur dioxide has penetrated into the absorbing-tower, the result being a reduction of nitrous acid and loss of nitre. On principle this is, of course, correct (comp. p. 627), but it is not certain whether the above amount is the real limit in all ordinary cases. Crowder also noticed that the proportion of oxygen in the gases issuing from the tower is always slightly larger (0·08 to 0·54 per cent.) than that passing in. The explanation of this phenomenon proposed by him, viz. the diminution of volume consequent upon the removal of SO_2 or some decomposition of the oxides of nitrogen, is altogether inadmissible; any chemical action of the SO_2 and the nitrogen oxides within the Gay-Lussac tower could only tend to diminish, not to increase, the amount of oxygen, and the shrinkage caused by the removal of those gases is far too slight to be observed in gas-analysis (it is, of course, useless to expect such gas-tests to give accurate results, even in the first decimal per cent.). I have little doubt that Crowder's observation was due to some air being drawn into the exit-tube by a slight leak or by the feeding-holes sucking in a little air; this is extremely probable, as the Gay-Lussac tower offers a very great resistance to the draught, and the inward suction at the exit-tube, as shown by an air-gauge, is consequently many times greater than that at the inlet-tube.

Attempts have been made, but hitherto entirely in vain, to absorb or utilize the last traces of acids in the exit-gases. Sometimes they are washed with water in a small coke-tower or plate-column, but this does not do much good.

Mitarnowski and Benker (French pat. 212,989) propose passing these gases through a solution of ferric sulphate, or through a column charged with granulated copper and fed with water, in order to produce sulphate of copper; but this will hardly pay, for the same reason as that which is at the bottom of the necessarily incomplete action of the Gay-Lussac tower.

A proposal made by Frémy to absorb the SO_2 in the exit-gases from the Gay-Lussac tower by a coke-tower fed with nitric acid is characterized by Sorel himself, who reports it ('Traité,' p. 314), as an absurdity, and an idea never likely to be carried out in practice, since there is trouble enough to keep back the nitrous vapours without creating them anew at the last. Frémy's designation "tour aéronitrique" is the only fine thing about this proposal.

Various plans for recovering the Nitre in other ways.

Merely for the sake of completeness it may be mentioned that several other plans have been proposed for utilizing the nitre-gas escaping from the chambers. Not one of these has ever possessed any practical value; and they can hardly be said to have even an historical interest, since they have never been employed except in a few isolated cases. Kuhlmann, for instance, employed 30 Woulfe's bottles, the first ten of which were filled with water, the second ten with a solution of barium nitrate, and the third ten with barium carbonate suspended in water; the mixture resulting in the last ten bottles was used in the second ten bottles, where barium sulphate ("permanent white" or "blanc fixe") was precipitated. Others have used milk of lime, ammoniacal liquor, or even pure water for the absorption of the acid vapours. All these plans are so very much less advantageous or complete than Gay-Lussac's process that they cannot at all compete with it.

G. Wachtel (Dingl. Journ. vol. ccxlv. p. 517) proposed forcing the exit-gases by means of a Körting's injector through a red-hot iron or fire-clay retort filled with iron-turnings. Here the nitre-gas is to be reduced to ammonia, which is to be absorbed by hydrochloric or sulphuric acid. Nobody seems to have been rash enough to make a practical trial of this plan.

DENITRATION OF THE NITROUS VITRIOL.

The operation going on in the Gay-Lussac towers whose final result is the production of an acid more or less charged with nitrous compounds, viz. the "nitrous vitriol," requires for its necessary complement another operation, by which the nitrous vitriol, which by itself has no practical use, can be reintroduced into the chamber-process, both in order that the absorbed nitrous compounds may be restored, and that the sulphuric acid originally employed may be recovered in a pure state. It cannot be denied that Gay-Lussac was not sufficiently successful in completing his invention (which has proved so important and useful in the manufacture of sulphuric acid) in this particular; and it is more than probable that the slow extension of his process, nay, even the far from exceptional abandonment of it where it had been introduced in the first instance, must be attributed to the fact that the denitration of the nitrous vitriol was attended with too many difficulties, expenses, and breakdowns of apparatus. The invention of the *Glover tower*, which does away with all this, must therefore be regarded as almost equally important as that of the Gay-Lussac tower itself; and in fact the *general* introduction of the latter only dates from the time when manufacturers were able to combine it with the Glover tower.

The various contrivances for denitrating nitrous vitriol were described and criticised thoroughly and in detail by Fr. Bode, in 1876, in a paper "On the Glover Tower," which obtained the great prize of the Berlin Society for the Promotion of Industry; and this essay has been used to a great extent in the following description. Bode's paper has also been published by instalments in 'Dingler's Journal,' vols. ccxxiii. to ccxxv.

The methods for denitrating nitrous vitriol are founded, on the one hand, on diluting it either with hot water or steam, or with a combination of both, and, on the other hand, on the action of sulphurous acid, mostly along with a certain amount of dilution. That in these cases the nitrososulphuric acid is completely decomposed, either by the dilution or the action of the sulphuric acid, has been proved in detail from theoretical investigations. We shall now treat of the apparatus and modes of procedure employed in practice for that purpose.

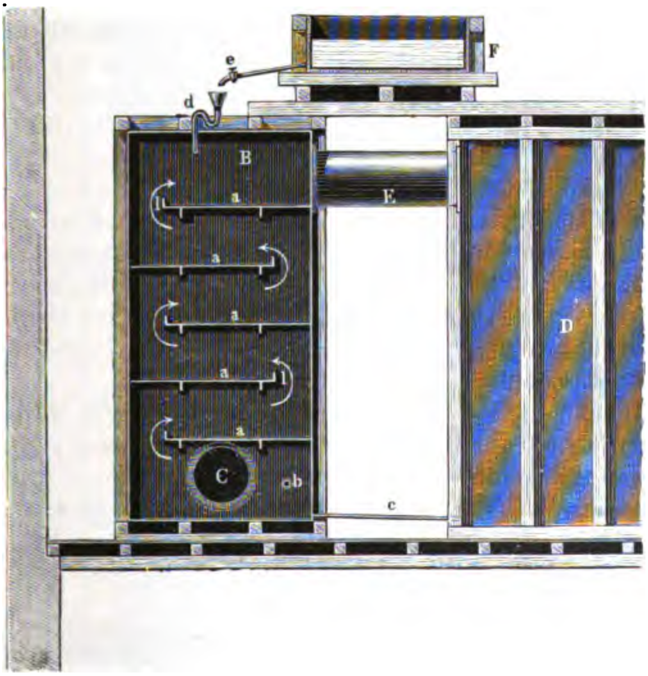
One of the oldest apparatus was described in Payen's 'Cimie Industrielle,' and has been copied from this into most text-books; it may be called the "shelf-apparatus."

It is shown in Fig. 281 and is easily understood: F tank for nitrous vitriol, *e* outlet-tap, *d* inlet-pipe, *a a* shelves with overflow-edge, *l*, which retains a 4-inch layer of acid on each shelf, C inlet for burner-gas, *b* steam-pipe, *c* outlet for denitrated acid into the lead chamber D, E outlet for nitrous fumes.

Another apparatus, constructed on the same principle as that just described, is the "Dénitrificateur" proposed by Gay-Lussac himself. It is a lead column of square or circular section, provided with a grating a little above the bottom, and packed with coke on the top of this. The nitrous acid runs in at the top, and is scattered by means of a rose. Below the grating the gas of the sulphur- or pyrites-burners enters and meets the nitrous vitriol descending; at the same time either a jet of steam is introduced separately, or the gas is previously conducted through tanks filled with water, in order to be saturated with moisture.

In these apparatus the denitration evidently takes place by the joint action of the steam and the sulphur dioxide. The acid ought to arrive at the bottom entirely free from nitrogen compounds; but it is then so dilute that it must be run back into the chambers. Such apparatus are not to be found in use in any place at the present day, for good reasons. Since the acid is in them diluted to the same extent as in the process of denitrating by hot water or steam alone, they present no advantage over the latter; indeed they were in the first instance replaced by the latter processes. But the apparatus just described have this drawback, that they last a very short time, on account of the rapid destruction of the lead. The destructive action is always very strong in the first chambers, which, even under the best conditions, and in the presence of a Glover tower, suffer more than the remaining chambers, and have to be made of thicker lead if they are to last as long. This is due partly to the heat of the gas, partly to the nitrous compounds themselves. It is evident that much more of this action must take place in a very

Fig. 281.



small chamber, such as the "shelf-apparatus" or Gay-Lussac's "Dénitrificateur." The worst, however, of these apparatus is that the steam introduced into them necessarily leads to the condensation of very dilute sulphuric acid and nitric acid on the sides of the apparatus, which must rapidly corrode the lead. Moreover, considering the small size of the chambers serving as shelf-apparatus or dénitrificateurs, any changes in the chamber-process, in the composition of the kiln-gas, of the supply of steam, of the outer temperature, &c. must be felt in them very much more than in a large lead chamber. Therefore, from time to time, stronger nitrous vitriol will condense on the walls, and be diluted directly after by an increased condensation of water, and thus become charged with nitric acid. As every practical man knows, the interior walls of a working lead chamber are always covered with a white slimy lining of lead sulphate, which retains acid like a sponge, but at the same time protects the lead from further action, until such time as the acid is diluted by condensed steam, gas is given off from it, and the slimy mass of lead sulphate is loosened and washed off, whereupon the lead is again exposed to fresh attacks. The older denitrating-apparatus, therefore, were exposed to very rapid destruction, because they employed the simultaneous action of sulphur dioxide and of steam, and were therefore soon abandoned.

In England, most manufacturers passed over to *diluting the nitrous vitriol* in separate small *boxes with water and steam*, whilst on the Continent usually "steam-columns" or "cascades" were preferred. The English arrangement, such as was almost general in former years, and has only been placed in the background by the Glover tower, is shown in fig. 282. *a* is a lead vessel, about 1 foot high and 18 inches wide, which stands within the lead chamber, very near the inlet for the kiln-gases. Three pipes, *b*, *c*, and *d*, lead into *a*, passing through the side of the chamber and burnt into it. Of these *b* conveys steam, *c* water, and *d* nitrous vitriol; *c* and *d* end in funnels, through which the liquids run. The steam comes from a steam-boiler. The vessel *a* is first filled with water; this is

Fig. 280.

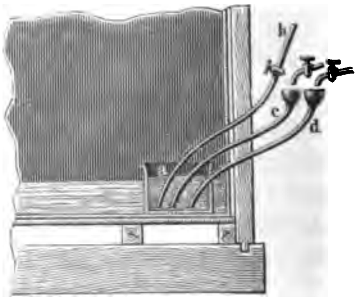
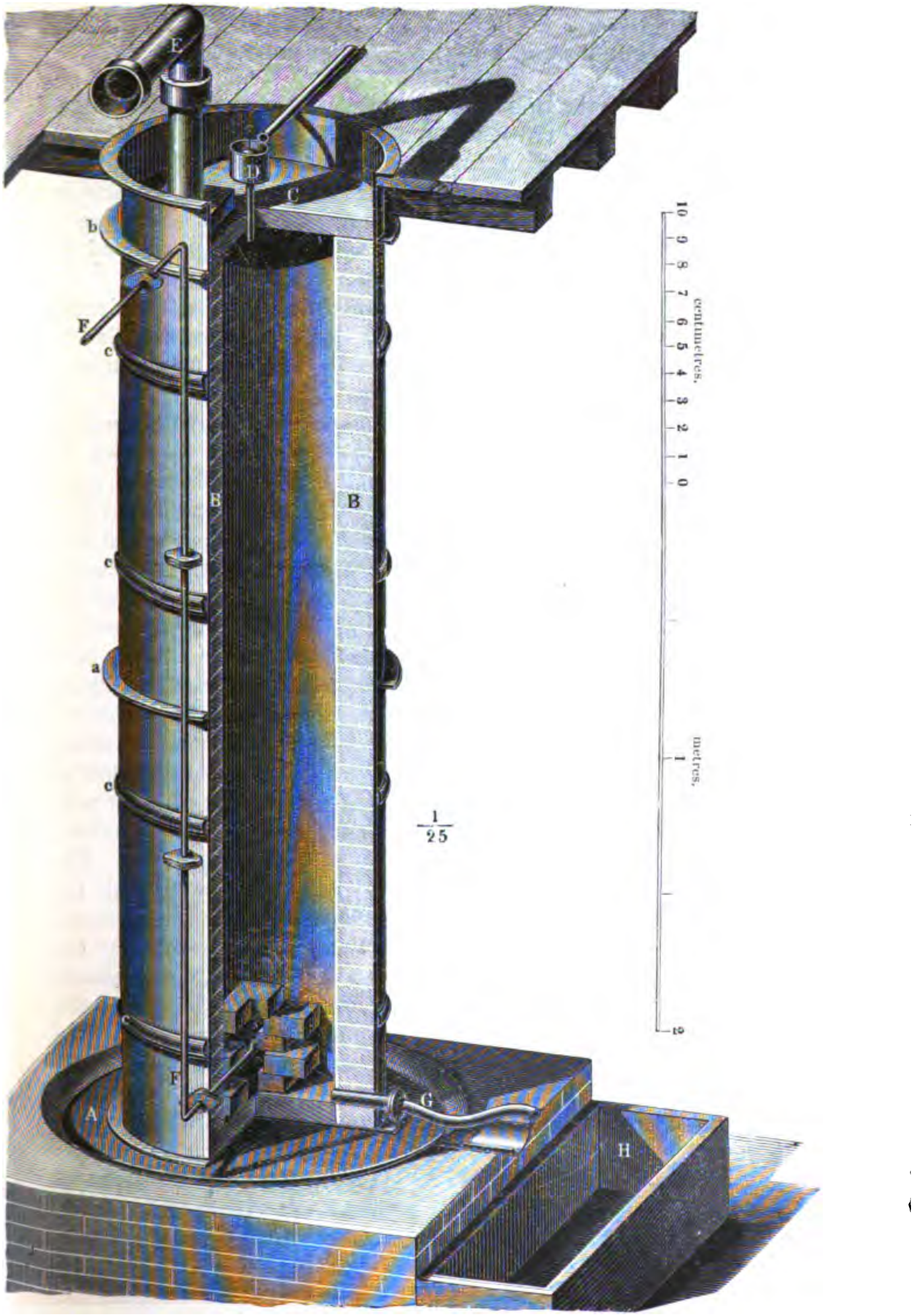


Fig. 283.



then heated to the boiling-point by steam; and now steam, water, and nitrous vitriol are admitted in such proportions that the latter is completely denitrated before it can run over out of the box *a*. The proximity of the gas coming from the pyrites-burners acts in this way: the escaping oxides of nitrogen are at once spread through the chamber and are mixed with the other gases; and at the same time the gas protects the lead against corrosion.

More perfect is the arrangement formerly usual on the Continent, where the denitration takes place on *cascades*, exactly similar to those described previously (p. 519), only with the addition of a contrivance for introducing hot water.

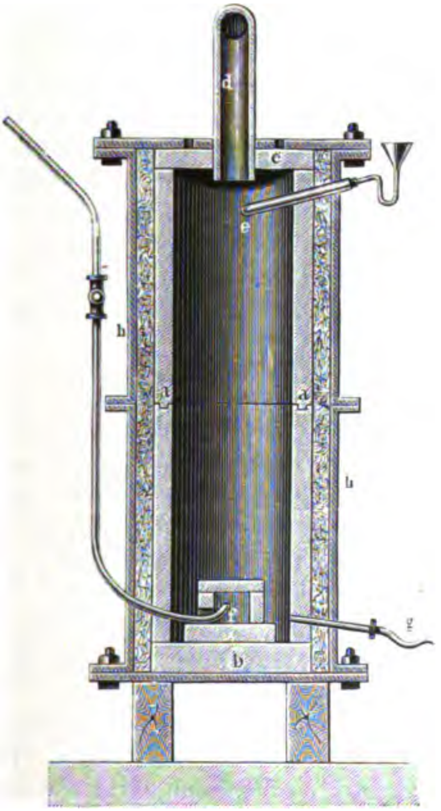
The *denitration by steam alone*, or by steam with very little water, takes place in the so-called *steam-column*, which is shown in fig. 283 on a scale of 1 : 25, as it was worked at Freiberg some time ago. It consists of a cylinder of strong sheet-lead, 11 feet 6 inches high, 3 feet wide, composed of three drums, joined at *a* and *b*, and strengthened by hoops. It is lined with acid-proof bricks, B, joined by a mortar made of fireclay and boiled tar [or of asbestos and silicate of soda, comp. pp. 120 & 619]. The bottom is formed by a lead plate A (or better a loose saucer), the top by a stoneware slab C. D is the feed-pipe for acid, E outlet for nitrous vapours, F steam-pipe, whose mouth is covered up and built round with bricks in such a way that proper channels remain for the steam and the acid. On the top of this the column is filled with bits of flint nearly up to its cover; they are about the size of a fist near the bottom, and decrease towards the top to the size of a walnut. In place of these some works use bits of broken stoneware. The nitrous vitriol running in at the top trickles down through the bits of flint, and is decomposed in this way by the rising steam. Whilst the nitrous acid given off from it goes away into the chamber through the pipe E in the state of vapour, the sulphuric acid, diluted by the condensed water, arrives at the bottom of the steam-column, and runs through the pipe G into the tank H. The pipe G is so bent as to remain always luted by the acid.

According to Bode, such a column, at Freiberg, sufficed for a system producing 126 cwt. of sulphuric acid of 170° Tw. in 24 hours.

In a large factory near Newcastle there existed, till 1873, steam-columns consisting of a cast-metal pipe 3 feet wide and 9 feet high, with a lining of lead and another lining, inside the first, of thin bricks (2 inches), and a packing of flints. Since then they have been replaced by a Glover tower.

There are also steam-columns made without a lead jacket; but they cannot in this case be built up of bricks, but must be made in one or two pieces. Bode shows such a column, erected by Dr. Gilbert at Hamburg (fig. 284). Its inner diameter is 1 foot 3½ inches, its height 13 feet 1 inch. It consists of two gas-retorts, *a a*, made tight at the joint, after heating the same, by asphalt. The bottom, *b*, and the cover, *c*, are formed of round fireclay-slabs; the latter contains an opening for the stoneware pipe *d* for carrying off the nitre-gas and the excess of steam into the chamber. The nitrous vitriol enters at *e*, the steam at *f*, and the denitrated

Fig. 284.



sulphuric acid runs off at *g*. The retorts are surrounded by the cylinders *h h*, of ½-inch cast iron, which are bolted together and to the cast-iron top and bottom plates. A space of 1¼ inch remains between the cast iron and fire-clay, and is filled with melted asphalt having a very high fusing-point. The column is filled with bits of flint; the mouth of the steam-pipe is protected by loose bricks. This apparatus in Bode's time had been in operation for five years without giving any trouble, and supplied a set of chambers making 6 tons of acid of 170° Tw. in 24 hours.

In other works the steam-columns are made much smaller, which is evidently quite sufficient. In Würtz's 'Dictionary of Chemistry,' iii. p. 157, Scheurer-Kestner figures a column made of a piece of Volvic lava 6 feet 6 inches high, and only 8 inches wide inside, 3 feet outside, filled with broken glass. The whole is surrounded by a lead casing. Such a column suffices for a chamber of 4000 cubic metres, turning out 8 tons O.V. per day. These Volvic columns seem to stand better than any other kind of steam-column, but they also crack sometimes.

As late as 1890 I found in Hamburg a steam-column of the following construction. It consisted of a cast-iron cylinder, lined with bricks inside; the bottom part, about 8 inches, was made of lead and dipped into a very thick cast-lead dish, forming a hydraulic lute, just at the point where the steam entered. The outflowing acid was kept at 112° Tw.; it tested on an average 0·05 per cent. N_2O_3 and 0·01 per cent. NO_3H, which seems very good work for that strength.

Bode asserts that the simplest and cheapest apparatus of this kind consists of ordinary stoneware receivers, as shown and described pp. 567–569 of our second edition. This kind of denitrating-apparatus does not appear to be in existence anywhere now; probably it would stand a very short time. We also refer to the same place for Bode's comparison of the efficiency of steam-columns, of cascades and stoneware receivers, as being devoid of actual interest at the present time.

In 1902, steam-columns were still used, at Freiburg, for denitrating nitrous vitriol. The reason for retaining these apparatus was that the gases at those works enter the chambers at the temperature of the surrounding air (comp. p. 394), and it was assumed that this is too low for working a Glover tower; but it is doubtful whether this assumption is correct (see later on).

Glover Towers.

The apparatus which is now used for denitration in all but exceptional cases is the *Glover tower*, which is properly treated in this Chapter, since its inventor had in the first instance constructed it for denitration, although it might just as well be described as a cooling and a concentrating apparatus. The Glover tower was invented by the late Mr. John Glover, of Wallsend, near Newcastle-on-Tyne. According to personal information received from Mr. Glover, he had already built his first tower in 1859, at the Washington Chemical Works, near Durham. This tower was made of fire-bricks and packed with a network of thin fire-tiles. It lasted a year and a half, and proved the correctness of the principle. In 1861 Glover, at the same place, built a lead tower; and when erecting another works at Wallsend in the same year, he, of course, built a similar tower there as well, which worked until 1863 or 1864. From the experience gained in this way, Glover constructed in 1864 a third tower, which, in all essential respects, was the same as is used to this day. Up to that time only his nearest neighbours had introduced the tower. It must here be observed that its inventor had not only taken out no patent for it, but, with great liberality, had shown it to every one interested in the matter. In spite of this, some of the manufacturers on the Tyne, intending to "improve" the tower, committed mistakes in its construction; and, at least in one case, this led to its being given up again, although it has since been reintroduced. Between 1868 and 1870 all the larger and better-managed works on the Tyne introduced the Glover tower; it was adopted in Lancashire about 1868, in London in 1870. Until 1871 nothing had been published about the Glover tower; and it was entirely unknown outside a limited number of English alkali-works till I published a paper on it in 'Dingler's Journal,' vol. cci. p. 341, which made it generally known, and led to its adoption, first in Germany, then elsewhere. Soon after my publication objections were raised against the tower as a denitration apparatus (nobody has ever doubted its excellence as a concentrating and cooling apparatus). The first objections raised by Bode (' Dingler's Journal,' ccii. p. 448) were immediately refuted by me (ib. p. 532), and have since been withdrawn by Bode himself. Bode has become one of the most zealous constructors and advocates of the Glover tower. Also the objections raised by M'Culloch (Chem. News, xxvii. p. 135) have been answered by Glover (ib. p. 152), by me (ib. p. 162), and Bode (Prize Essay, p. 5). M'Culloch himself afterwards changed his opinion. Much more serious objections have been made by Kuhlmann (Hofmann's Official Report on the London Exhibition of 1862, p. 174) and by Vorster ('Dingler's Journal,' ccxiii. p. 506), on the assumption that the contact of hot sulphur dioxide and nitrous vitriol in the tower causes a considerable loss of nitre compounds in the shape of nitrous oxide or of free nitrogen. It is certainly a fact that, under certain conditions, hot sulphur dioxide reduces the nitrogen oxides down to nitrous oxide or even to nitrogen. But that such conditions exist in the Glover tower Kuhlmann could not prove, because he had none at his disposal; nor did Vorster experiment with the tower itself in this direction, although he made other interesting observations respecting it; but, entirely on the strength of laboratory experiments, he asserted that 40 to 70 per cent. of the nitrous compounds were lost in the Glover tower. His experiments, however, were made under totally different conditions from those existing in the Glover tower; and I succeeded in refuting Vorster's inferences on the loss of nitre from his own figures ('Dingler's Journal,' ccxv. p. 56, ccxvi. p. 79). In the experiment considered by Vorster the most conclusive, he passed hot sulphur dioxide mixed with air for 27 minutes through nitrous vitriol heated to 180° C.; and it is inconceivable how he could assert that this condition answers to that in the Glover tower. Into this the nitrous vitriol enters quite cold, mixed with chamber-acid; and only on leaving, when its heat is greatest, does it attain 130° C. It is out of the question that it should have that temperature in any considerable part of the tower, much less 180°, as in Vorster's experiment. On the contrary, that acid which shows a rather elevated temperature (but never anything like so high as in Vorster's experiments) contains next to no nitrous acid, but is only further concentrated by hot kiln-gas; and, at all events, the denitration takes place to the greatest extent in the upper part of the tower, where the acid is still pretty cold. This follows with certainty from the well-known fact that the denitration of dilute acid takes place readily, that of concentrated acid with great difficulty. Apart from this, the acid is never exposed to the current of hot sulphur dioxide so long as in Vorster's experiments. If once the packing has been quite impregnated, the acid gets from the top to the bottom in a few minutes; but owing to its fine division, it is almost entirely denitrated near the top. In short, Vorster's experiments are useless for deciding the matter in question, even if they were not refuted by the plain fact, that with the Glover tower the waste of nitre is *at least* no greater than with any other process. This subject is noticed more fully below.

Subsequently (Berichte der deutschen chem. Gesellsch. x. p. 1432—more explicitly in 'Dingler's Journal,' 1877, ccxxv. p. 474) I criticised in detail the experiments and statements of Kuhlmann and Vorster, and proved their irrelevancy. I further proved by experiments that if the sulphur dioxide is mixed with a similar excess of oxygen as in the kiln-gas, this mixture decomposes nitrous vitriol, even at a temperature of 200° (in the Glover tower it never gets beyond 130°), in such a way that the *whole* of the nitrogen oxides can be recovered by absorption in concentrated sulphuric acid. Pure sulphur dioxide, free from oxygen, does not act on nitrous vitriol at 110°–130°, but only at 200° C., in such a way as to cause the formation of some nitrous oxide. This, however, is not a practical case at all; and it is certain that in the Glover tower neither nitrous oxide nor nitrogen is formed in appreciable quantities. My experiments and calculations were attacked as inacurate by Hurter ('Dingler's Journal,' ccxxvii. pp. 465 & 563), but were completely vindicated by me (ib. ccxxviii. pp. 70 & 152)

If there were any truth whatever in Kuhlmann's and Vorster's assertions, it would certainly be a cause of still greater loss when the fresh supply of nitre-gas is carried through the tower, as is done in the great majority of English, or when even the liquid nitric acid is run through it, as in most continental works. Then not merely 70 per cent. of the nitrous vitriol, but also 70 per cent. of the fresh supply of nitre, or nitric acid, would be wasted by the tower. This certainly would be felt in a very sensible manner. But already in 1871, of the ten works on the river Tyne which possessed Glover towers, only three worked so as to decompose the nitre by the gas of separate pyrites-burners, and to take the gaseous mixture past the Glover tower direct into the chambers. The other seven works sent the gas of *all* burners, along with all the fresh nitre-gas, through the towers, *without consuming any more nitre* than the three former ones. Among these three works was that managed by myself, and in my first publication I recommended this arrangement. Later on, from experience gained in the meantime, the plant was altered, and *all* the kiln-gas, along with the nitre-gas, was taken into the Glover tower; but no extra consumption of nitre whatever could be detected. In the same way Mr. Schaffner, of Aussig, found no extra consumption ensue when he began introducing all the liquid nitric acid through the Glover tower. Comp. *suprà*, p. 522.

It is absolutely certain, from the practical experience of many works, that with the Glover tower rather less nitre (never more) is used than with steam-columns or cascades. This is corroborated, for instance, by the former opponent of the Glover tower, Bode, in 'Dingler's Journal,' ccxvii. p. 305, and in his prize essay, p. 87; and, altogether, no contrary statements of those who have had practical experience of the tower have been made known. On the contrary, the Glover tower has not only been generally accepted in England, but also on the Continent. Already in 1875 the Berlin Society for the Promotion of Industry offered a prize for an essay on this subject, in which the utility of the Glover tower for most cases is expressly presupposed, and only its applicability for kiln-gas of inferior heat is mentioned as doubtful and requiring examination. The result of this was Bode's often-mentioned essay on the Glover tower. At the present day the Glover tower forms an essential part of every well-arranged sulphuric-acid works, and ranks with the Gay-Lussac tower. Certainly it will not answer to expectations when constructed in an improper way or with unsuitable material, and therefore, at first, its use was here and there discontinued; but the same may be said of every apparatus used in the whole range of industry; and the *consensus* of the great majority of manufacturers has entirely decided *for* the Glover tower. Bräuning (Zsch. J. Bergwesen, etc., 1877, p. 140) also quotes the experience of a whole series of works at Oker in which the tower is employed, and where, since its introduction, less nitre is used than before, in consequence of the acid being completely denitrated, so that no loss can be incurred through the reduction of nitric acid to nitrogen or nitrous oxide. During my extensive tours through a number of the best English, German, and French alkali-works, I have everywhere received the same information, viz. that since the introduction of the Glover tower less acid is consumed than formerly (with the diluting process). This may very frequently be in consequence of the chamber-acid being also denitrated in the Glover tower; but in some works the acid of the large (or first) chamber is not kept nitrous at all, and in others, from various causes, only a small portion of the chamber-acid passes through the Glover tower. In no case is there the slightest reason for asserting that the Glover tower, by itself, wastes more nitre than the diluting process. At Malétra's works at Rouen, before the introduction of the Glover tower, 2 parts, since then only 1·3 part of nitre has been used to 100 parts of pyrites.

Hurter himself, in 1877, when he still imagined that a considerable portion of the nitrous gases was reduced to N_2O and elementary N in the Glover tower, admitted that "with careful work" there was no more nitre used after the introduction of the Glover tower than before, as quoted by Jurisch ('Schwefelsäurefabrikation,' p. 153), whose continued adhesion to the long exploded belief in such a destructive action of the Glover tower has been already mentioned in the 6th Chapter, p. 522, and which is probably the last survival of that error. It should be noticed that Hurter, in his many years' position as chief chemist of the United Alkali Company, has never made any attempt at doing away with the Glover towers, formerly condemned by him as destroyers of nitre.

Gay-Lussac himself had at first denitrated the nitrous vitriol by burner-gas *and steam* (p. 632); much later again Cl. Winkler, in 1867 ('Untersuchungen,' etc., p. 24), proposed very clearly the denitration of nitrous vitriol by sulphur dioxide, without being aware of the fact that this plan had been carried out for some years in practice by Glover and others. But these attempts were vitiated by the proposal to add steam or water, and they did not embrace the concentrating action of the apparatus which is now called the Glover tower.

Functions of the Glover Tower.—Although outwardly resembling a Gay-Lussac tower, the function of the Glover tower is exactly the opposite—viz. to deprive the nitrous vitriol running off *at the bottom* of the Gay-Lussac tower of its nitrous compounds, and to restore it to a proper state of concentration for applying it again *at the top* of that tower. This, certainly, is only one of the functions of the Glover tower, but the most important and characteristic of all. The tower fulfils this function by exposing the nitrous vitriol, usually mixed with chamber-acid, in a finely divided form, to the action of the hot burner-gas, whose heat acts concentratingly upon the sulphuric acid, and whose sulphur dioxide acts denitratingly upon the nitroso-sulphuric acid; and the simultaneous concentration and action of the sulphur dioxide seem very much to advance the denitration, which takes place according to the equation:

$$2SO_2(OH)(ONO)+SO_2+2H_2O=3H_2SO_4+2NO.$$

Glover's apparatus cannot be put in the same line with the apparatus described above (p. 632 *et seq.*), because in it no condensation of dilute sulphuric acid containing nitric acid can take place on the lead walls, and because it is altogether so constructed that the lead nowhere comes into contact with the hot gas and the nitrous vitriol. Once properly built, it continues working for many years, and causes no interruption of the process. Besides, it possesses two very great advantages. The first is, that it is both the most complete and the most rational of all cooling-contrivances for the burner-gas:—the most complete, because the gas is brought into immediate contact with the cooling-liquid in the shape of a fine spray, not separated from it by a metallic wall or only exposed to the cooling-action at the circumference of the current; the most rational, because no expense has to be incurred for pumping up cold water for cooling, but the generated steam is at once usefully employed in the chamber. The second and still greater advantage of the Glover tower is that in it not only all the acid serving for absorption in the Gay-Lussac tower, but the whole of the chamber-acid is brought to 144° or even up to 152° Tw. without any expense except that of pumping the acid to the top of the tower—an expense which is very small indeed, especially in the case mentioned on pp. 531 & 606, where the exhaust-steam of the air-pumping engine is used as steam for the chambers.

The Glover tower is, moreover, now mostly used for introducing the requisite fresh nitric acid into the chambers without any special apparatus, by running it down along with the nitrous vitriol. Before it arrives at the bottom it is fully denitrated, as well as the nitrous vitriol itself (comp. Chapt. V. p. 522).

Even a solution of nitrate of soda has been employed in a similar way, but this has been given up as impracticable (p. 528).

Construction of a Glover Tower.

The constructive principle of the Glover tower is this: to provide an apparatus, perfectly tight against liquids and gases, and at the same time capable of resisting both heat and the action of strong acids in the liquid and gaseous form. A gas-tight apparatus is preferably made of some metal, and this principle is followed in the construction of vitriol-chambers. But lead, the only metal to be thought of, does not resist the action of hot acid gases at temperatures not very far removed from its melting-point. Acid-proof material of any other kind requires making joints with some mortar or cement, none of which again is sufficiently resisting in this case. The solution of the difficulty is attained in this way:—An outer shell of lead, constructed as usual in the case of chambers, towers, and the like, is provided with an acid-proof stone or brick lining, *without any mortar*. The latter, which would be destroyed directly, is not necessary for the stability of the erection if it is properly designed, nor need the lining be gas-tight, as the small amount of gas which finds its way through the joints is sufficiently cooled down not to do any harm. Nor can the lining itself, which is always a bad conductor of heat, transmit enough heat to be dangerous to the lead.

We now come to the question as to what *lining* should be employed. Undoubtedly the best material for this purpose is *Volvic lava* (see p. 583), which resists both acids and heat better than any other material so far known. It occurs near Clermont-Ferrand, in the centre of France, and can be had in large blocks which are easily shaped to design, *e. g.* from Brosson Lafilichat frères, or from A. Moity, both residing at Volvic (Puy-de-Dôme). In 1880 the cubic metre cost 60 francs; the lining of a large Glover tower, as will subsequently be described, cost 4500 francs (say £180).

Next to this, where Volvic lava is considered too dear or difficult to procure, comes "chemical" brick or stoneware, *i. e.* such as resists the acids and also the heat up to the required extent, but it need not be "fire-brick" proper. None of these bricks last for ever, and they always yield some alumina to the acid, but they may serve for several years.

In Great Britain the "blue bricks" of Mold in Flintshire are usually employed for lining Glover towers. The following is the composition of the best class called "metalline," supplied by the Buckley Brick and Tile Company, according to 'Chemical Trade Journal,' x. p. 46:—63·01 SiO_2, 25·95 Al_2O_3, 6·49 Fe_2O_3, 0·75 Mn_3O_4, 0·83 CaO, 0·40 MgO, trace of Na_2O, 2·57 K_2O, 0·9 organic substance, and water.

In Germany the bricks made at Bad Nauheim, at Bendorf near Coburg, and at Aussig are mostly used.

The manufacture of acid-proof bricks for Glover towers, according to 'Thonindustrie-Zeitung,' 1890, p. 642, requires clay rich in silica more than in alumina, of a dense, non-porous character. Some descriptions of clay which are almost free from iron and can be burned to a clinker can be used directly. Where no such clay is available an artificial porcelain-like mixture can be made with from 25 to 30 parts felspar, 25 to 30 best China-clay or other good fire-proof clay, and 40 to 50 parts quartz. It should be burnt to a clinker, and should not shrink too much in the process. The bricks are best covered with a glaze consisting of 54 parts quartz, 84 felspar, 35 ground chalk, and 26 ground China-clay.

The "packing" of the Glover tower is made of similar material to the lining, but this will be treated later on (p. 653).

We shall now explain the principles of constructing the various parts of a Glover tower.

The *foundation* of a Glover tower used to be made of strong brick pillars, with a roof formed by a strong brick arch and braced together with iron stays and rods. The pillars may also be joined by strong railway rails, instead of an arch, and they may be themselves constructed of cast iron, which makes the foundation much lighter and more accessible. The top of the foundation is covered by a lead apron 6 or 7 lbs. to the square foot, for the purpose of protecting it against acid drippings. This apron may be turned up so as to form a saucer with an overflow spout; and if this be kept full of water it will help to preserve the inner saucer, by keeping this at a moderate temperature.

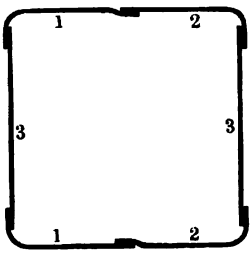
Sometimes the platform at the top of the foundation is covered with a molten mixture of pitch and brimstone, and the leaden apron is put upon this while still warm. This is an absolute protection against any corrosion of the iron pillars and girders by any acid finding its way down.

The *frame* of the tower must, of course, be different according to whether the tower is angular or circular in section. The former kind will be made clear by the designs shown later on; the latter is distinctly seen in the section of a French Glover tower, lined with Volvic lava, given below.

The material of the frame is mostly wood, preferably pitch-pine, but iron frames are very appropriate in this case. In both cases the frame has to support the acid tanks required for feeding the tower, and also the light shed covering the top.

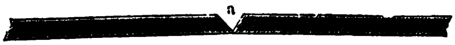
The *tower itself* is made of 14-lb. lead, its bottom of 35-lb. lead, the straps of 9-lb. lead. Its sides are suspended from the top and side joists, just like those of a chamber. The lead stands a little off the wood, which is of importance for the protection of both the wood and the lead. In order to avoid seams at the corners, where they would be weakest and where they could not be very well repaired on account of the frame, two of the sides are made of two sheets of lead (1, 2, fig. 285) each, which are burnt together in the middle, and which reach round the corners, where the sheets 3 are burnt to them. The seams are best burnt outside. All the side sheets reach down from the top to the bottom without any horizontal seams, and hang loosely within the saucer.

Fig. 285.



Sometimes even square or oblong towers are not made in this way, but are constructed in single drums, like the circular towers (*vide infrà*), the higher one always resting on the bevelled-out edge of the lower. This is especially done where the tower-lead is not fastened to the ordinary frame by straps, but is held together by iron rings or closely touching wooden frames, which offer resistance to the thrust of the lining and packing. Iron hoops, however, have the disadvantage of gradually cutting into the lead, and closely-touching wooden frames cause the lead to be wasted much more quickly (p. 438).

Fig. 286.



The bottom saucer is formed of two sheets of lead burnt together in the middle and turned up all round to a height of 12 inches. Since sheets of 35 lb. to the square foot cannot be burnt together in the usual way, they are joined thus: they are placed close together, after having the edges cut off slantingly and scraped clean (fig. 286); into the rebate, *a*, thus formed, lead heated a good deal beyond its melting-point is poured: the latter, before solidifying itself, fuses the margins of *a*; and this is further assisted by a red-hot iron, so that the whole unites into a solid mass.

Another method of joining such thick sheets of lead is this: cutting the lead as shown in fig. 286, then heating the borders with a hot iron, and at once applying the blow-pipe so that the lead at this place melts for a certain depth and runs to the bottom of the triangular channel between the two sheets and closes this up, whereupon the whole channel is filled up by heating with the blow-pipe both the borders and a thick strip of lead, as usual when burning horizontal lead seams (p. 436).

Sometimes, as we have seen above, the bottom of the tower stands in another saucer, filled with water, which is allowed to get hot, but even in this state forms a protection to the inner saucer against overheating. In other cases there is a constant flow of cold water round the bottom saucer, so that the acid gets cooled to some extent before running away, which is an additional advantage. Another plan for cooling the bottom is that which is shown in the designs below, viz. arranging a network of air-channels in the brickwork underneath the lead bottom.

Inside the tower bottom is protected by a layer of 3-inch acid-proof slabs; sometimes first a piece of lead is laid loose on the bottom before putting the slabs on.

Lastly, we must notice the "*lip*," where the lead side of the saucer is turned over to form a place for the acid to run off continually into a leaden spout. This part, over which hot acid is incessantly running, and which cannot remain covered by a protecting layer of lead sulphate, is exposed to very great wear and tear; and as it cannot well be repaired while the tower is at work, the plumber must not neglect to put a false lip, consisting of a piece of sheet-lead beaten down close upon the real lip. The acid will then run over the false lip; and the latter, when worn out, can be replaced by a fresh piece in a few minutes.

Instead of a "lip," a lead tube of about 1¼ inch bore can be burnt in the side of the saucer, a little below its upper edge; but the plumber must do this with the utmost care, and make the joint extremely strong, in order to save repairs, which can only be done by stopping the work. At Stolberg, where the Glover tower has no saucer, but the bottom and the sides are in one piece, two running-off pipes are provided, so that one can serve when the other is stopped up. &c.

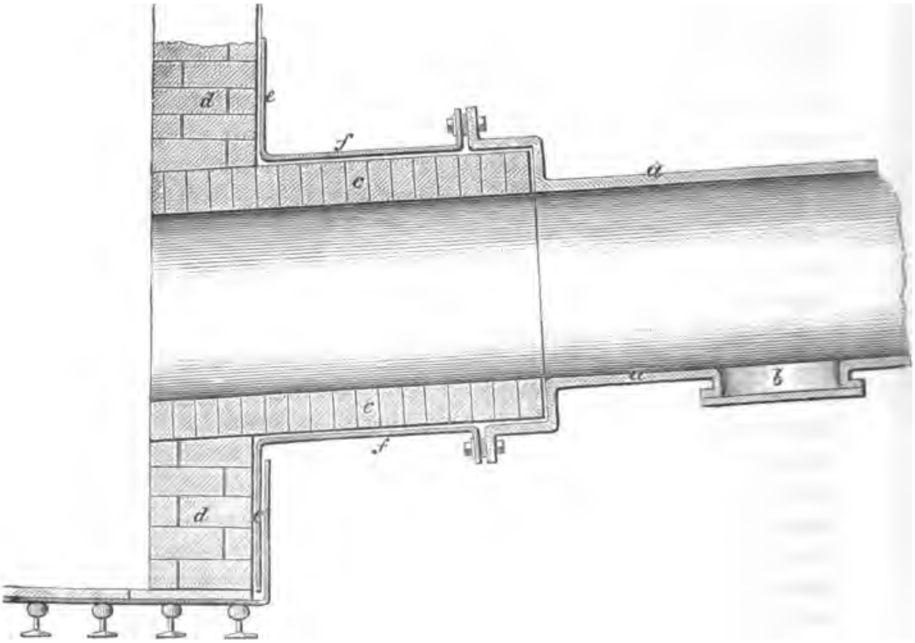
The *lead top of the tower* is suspended from wooden or, better, iron rails, to which it is fastened by straps, and which are supported by the side frame. Towards the centre it is dished out so that any acid leaking from the tanks cannot run down the sides of the tower, but finds its way into the tower through the hydraulic joints of the acid-distributor.

The *inlet and outlet of the gas* require special care. About the outlet nothing need be said, except that on its bottom a small ledge is formed, which compels the acid squirted into it to run back into the tower; this pipe also usually rises a little towards the chamber. On the other hand, the fixing of the entrance-pipe, which ought to have a slight fall towards the tower, is not quite such a simple matter, and at first caused much difficulty. It is mostly made of cast iron, and has in the great majority of acid-works, except in the above-mentioned cases, a temperature of at least 300° C. The lead of the tower, where it touches the cast iron, will therefore be quickly wasted, and any kind of cement put between the two will not do much good; in most works a little gas was seen escaping at this joint, and it gave occasion for many repairs. The following arrangement obviates this drawback :—The pipe is not at all in contact with the lead, but with a metal casting. The latter is in the shape of a ring with two flanges perpendicular to the plane of the ring; the thickness of the metal is 1 inch, the clear space between the flanges 4 inches, the total height 8 inches, the inner diameter of the ring 2 feet 9½ inches. Since the outside diameter of the inner pipe is 2 feet 7½ inches, there is a caulking-joint of 1 inch left free all round, which can be filled up with any hard cement—for instance, the ordinary rust-cement made of iron filings, sulphur, and sal ammoniac; this cement can be rammed in hard, as it lies between two iron surfaces. In the side of the tower, in the place in question, there is a circular hole to the circumference of which an upstanding flange is burnt, fitting the outer circumference of the cast-iron ring; between the lead and the iron a little ordinary tar and fire-clay cement is put; and a wrought-iron hoop in two parts with screw joints firmly binds together lead, cement, and cast iron. Since the outer part of the ring is cooled by the air circulating in the hollow space, only a small part of the heat can be communicated to it, which the inner part of the ring receives (already weakened by the layer of cement) from the inner pipe;

and therefore no difficulty is experienced in keeping the joint between lead and iron tight.

At the Aussig works the difficulty is obviated by attaching to the cast-iron gas-pipe coming from the burners a short piece of fire-clay pipe with a flange joint; the latter projects into the Glover tower; and the lead side of this is simply joined to the fire-clay pipe by a burnt-on flange surrounding the pipe, with tar cement between, and with an iron hoop pressing the lead flange onto the pipe. As the fire-clay pipe has much thicker walls, and is a much worse conductor for heat than a cast-iron one, this joint keeps tight even without the air-cooling just described.

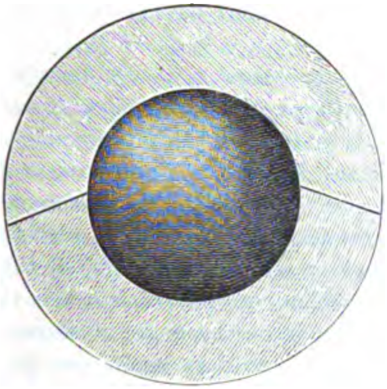
Fig. 287.



The plan followed at Griesheim with perfect success is shown in fig. 287. The burner-pipe *a a* (which at *b* shows a cleaning-hole at the bottom) is enlarged at its end, so that it embraces one end of the dry-walled annular-shaped brick flue *c c*, whilst the other end is tightly held in the brick lining *d d* of the tower. The lead side of the latter (*e e*) is continued into a lead cylinder (*f f*) surrounding the free portion of the flue *c c*; its end is bent round in the shape of a flange, pressed against a flange of *a a* by means of an iron hoop and screw-bolts; and the joint is made tight by asbestos packing.

At some works the burner-gas is carried into the tower by means of pipes, made of Volvic lava, in two halves, as shown in fig. 288. In this case no special contrivance is required for protecting the lead at the joint.

Fig. 288.



Duggan (E. P. 5012, 1896) employs a water-cooling jacket to the inlet-pipe for the Glover tower.

The *lining* of the tower is made of the materials described above, p. 645, and is so constructed as to serve at the same time as a support for the packing. This is facilitated by the fact that at the bottom, where the hot burner-gas enters, the lining must be anyhow much thicker than higher up, say 2 feet 3 inches all round. This is continued, say, 4 feet high, where the thickness of the lining diminishes to 18 inches; the recess thus formed serves, together with a central pillar, for supporting stone slabs which form a grid for the packing. Or else arches are sprung from side to side for the purpose of forming a grid, as shown in the designs below, by being levelled to a plane surface at the top.

Higher up the thickness of the lining decreases to 14 inches and at last to 9 inches.

The whole lining of the tower as well as the dome (arch) of the grid must be walled *dry*, without mortar of any kind (p. 645). In order to make the arch sufficiently stable without any mortar, it should not be made of ordinary fire-bricks cut or moulded to shape, but of large fire-clay lumps expressly manufactured for the purpose, whose sides join smoothly together. In some works all the bricks of the lining are ground upon one another, so that only extremely small joints remain. This is most easily done where the lining consists only of a few large blocks of Volvic lava (see p. 645, and below).

It is not considered bad work if the lining of a Glover tower stands for three years without having to be renewed; sometimes it stands much longer.

The *packing* of Glover towers in England usually consists of flints, picked from the chalk and purified by washing with hydrochloric acid. This material is absolutely acid-resisting and does not fly by the heat; but it does not possess any great surface, and it is very heavy. For the latter reason in many places the upper third of the tower used to be filled with the very hardest of coke; but this led to several accidents, by the coke taking fire when there was by chance no feed of acid on; there is also always some action of the acid on the coke, as shown pp. 231 and 585. Most factories have given it up again, but it may be still in use here and there.

Silica in the form of quartz is frequently employed; but some descriptions of it are very liable to cracking in course of time, and filling up the gas-channels to such an extent that the draught, and with it the yield, is enormously impaired. Herreshoff (U.S. P. 335,699; E. P. 1861, of 1886) employs nothing but pieces of quartz within the Glover tower. As these cannot be very well obtained in the regular shape for an ordinary lining, he keeps the lining a foot or so away from the side of the tower, and fills the space thus formed with quartz-sand. His system has met with great success in America, of course carefully selecting a suitable quality. Falding recommends quartz of a vitreous appearance, free from cleavage-lines and admixture with schist or other foreign matter. A little pyrites or oxidized pyrites does not hurt, but it must not be present in such quantity as to cause a flaw or to cause the quartz to "break down."

For packing the towers even broken glass or stoneware seltzer-water bottles with their bottoms knocked out have been found useful. One of the best materials for this purpose seems to be that supplied by the potteries at Bad Nauheim (Germany). It consists of almost pure silica, is burnt at the intensest white heat, cuts glass, and resists both any change of temperature and the prolonged attack of hot acids. Lining-bricks of this material cost £1 10*s*. per ton; for packing the towers short open cylinders are made about 5 or 6 inches long and 4 inches wide (at £3 10*s*. per ton). Formerly these were thrown in without any special care, but this is decidedly wrong; the cylinders should be put in in a regular way (see below). The Buckley Brick & Tile Co. also supply such "rings" for packing Glover towers. Mr. G. E. Davis informs me that this packing answers better than the coke-packing (which for Glover towers is most objectionable anyhow!), but the damper must be used more freely and the distribution of the acid must be more perfect than with coke.

Sometimes the Glover towers are simply packed with bricks, set on edge, in open work, as in a Siemens's recuperator. These bricks should of course resist the action of the acid. Blue Welsh bricks (p. 645) are frequently employed, and even some descriptions of common bricks seem to stand very well (J. Soc. Chem. Ind. 1885, p. 33). But undoubtedly they are always acted upon more or less, and yield up more iron and alumina to the Glover acid than towers lined and packed with Volvic lava or quartz (see end of this Chapter).

At Stolberg (1902) it has been found that acid-proof bricks, made from ground clay-slate in the Ruhr district, stand much better in the Glover tower than fire-clay cylinders. The hydrogen fluoride evolved in roasting blende acts most injuriously.

Brick-packing and also the ordinary cylinders have the drawback that they do not spread the acid or divide the gaseous current as well as denser kinds of packing.

Knab (Germ. pat. 67,085) promotes the unimpeded transit of the gases and prevents obstructions by a special kind of packing. He forms in the centre of the tower a column consisting of superposed cylinders. Each cylinder is provided with six slightly inclined earthenware tubes, arranged star-shape, and with their outer ends reaching into the brick lining of the tower. These stars are alternately arranged so that the pipes form a kind of steps, and four superposed stars fill up the whole section, the pipes of the fifth star lying exactly over those of the first star, and so on. The acid is thus compelled to run all round the pipes and to splash on to the pipes lying below. The pipes have different inclinations, in order to better divide the acid. [Such pipes will soon crack, and the whole apparatus then collapses.]

Saunders (U.S. P. 144,928, of 1873) employs hollow glass balls with one or more openings.

The *perforated plates*, on Lunge and Rohrmann's system, which have been described on pp. 478 & 586, are not very well adapted for packing a whole Glover tower; in the lower part the holes would be too quickly stopped up by flue-dust, and they would be liable to crack there as well. But they can be employed very well in the upper half of the tower, the lower half being packed with bricks set edgeways &c. This plan obviates an objection made to the Nauheim cylinders, viz. that in consequence of their comparatively large size the acid and the gases are not sufficiently brought into contact and the denitration is not very perfect.

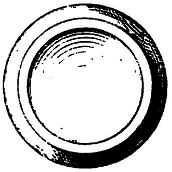
An excellent application of these plates has been made in a case where it was necessary to bring about the denitration at the lowest possible temperature, in order to avoid losses by the ammonia present in the gas-sulphur (spent oxide) employed. A small tower of only 13 layers of plates is put on the top of the ordinary Glover tower; the gases leave the latter at 90° C., and the plate-tower at 60° C. In spite of this slight difference of temperature and of the small height of the plate-tower, it was found to perform 80 per cent. of the denitrating work. Hence the plate-towers must be considered excellently adapted for this class of work, if they can be kept clear of flue-dust (which in the above case was retained by the old Glover tower). They must, however, not be flushed out while hot with cold water, which causes the plates to crack (comp. also p. 655).

Even when employing some other kind of packing than bricks (such as flints, cylinders, and the like) it is advisable to place just over the dome two courses of the same kind of bricks as serve for the lining, pigeonhole-wise, in order to divide the current of gas in a regular way. The packing, of course, must be done as systematically and carefully as that of the Gay-Lussac tower.

Lüty (Zsch. angew. Ch. 1896, p. 645) states that the quartz (or flint) packing formerly used in Glover towers has been entirely replaced in Germany, first by acid-proof bricks or slabs, since about 1880 by cylinders, about 5 in. wide, 6 in. high, and

$\frac{3}{4}$ thick. With quartz packing only 12 or 15 per cent. (after some mud has formed, only 10 per cent.) of the tower is empty and free for the reactions, with bricks about 35 per cent., with cylinders up to 58 per cent. Horizontal surfaces are much less active than perpendicular ones, which are in contact with constantly renewed acid. For this reason the success of the bricks and slabs is not so great as was expected, no more than that of the Bettenhausen "dividing-cones" ("Vertheilungskegel"), as shown in figs. 289 & 290. But the packing with ordinary cylinders has also led to many disappointments. This is easy to understand if the cylinders are glazed, or if they are placed in such a position that a system of continuous pipes is formed.

Fig. 289.



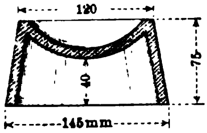
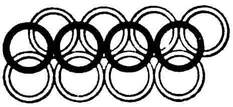


Fig. 290.

Fig. 291.



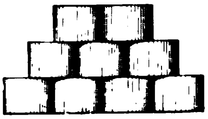


Fig. 292.

Lüty recommended cylinders 160 mm. high, 120 mm. wide, with walls 20 mm. thick, and a rough surface, placed in such manner that the joints are broken (figs. 291 & 292)*. They ought to be made of really acid-proof stoneware, not merely protected by a glaze which does not last very long. Even the best material, however, will be destroyed if improperly treated, especially by washing the tower with cold water, when its temperature is about 200° C. Instead of this, the tower should be allowed to cool down, or else hot acid or hot water should be employed for washing. When a tower has to be stopped for repairs to the chambers, the air should be prevented from entering, because the moisture contained in it, by diluting the acid soaked up by the cylinders, will in consequence of increasing the volume mechanically disintegrate these, even when no chemical attack of the earthenware takes place. The tower should not be washed with water at the beginning of the stoppage.

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* Niedenführ greatly prefers to this arrangement that which is shown in fig. 250, where each cylinder is placed at the intersection lines of *four* other cylinders.

At one time cylinders (rings) met with very much favour in German works and were regularly employed both for Gay-Lussac and Glover towers; but they have been in many places discarded again, because they do not divide the liquid on sufficiently extended surfaces, so that the contact between gas and liquid is imperfect and the towers have to be made very wide and high to fulfill their object. This is to a great extent remedied by a special kind of packing, designed by Niedenführ on the plan of the Lunge-Rohrmann plates, and shown in figs. 293 to 296. Here the acid is retained on the surface in a shallow layer, and on dropping down is always spread over fresh surfaces, without the danger of the cracking of plates and the stopping up of holes inherent to the ordinary Lunge plates (p. 654).

Fig. 293.

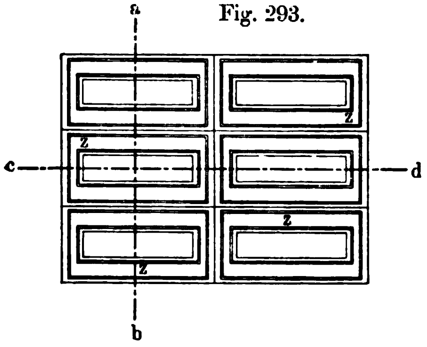
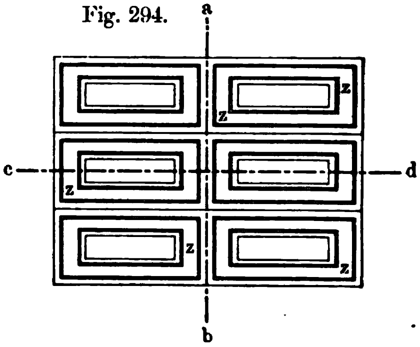


Fig. 294.



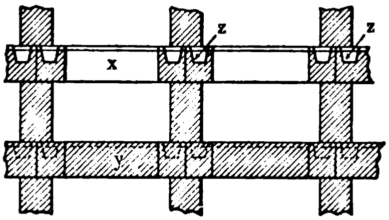


Fig. 295.

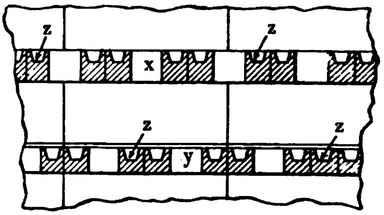


Fig. 296.

Official information received from the Oker works in 1902 confirms that since 1900 the quartz-packing of the Glover towers has been replaced by "Lunge-Rohrmann" packing of the kind just described and by dishes, with entire success as to the concentration and denitration of the acid. The acid issues at a temperature of 150° to 160°, the gases at 75° to 80° C. The towers receive per annum 21,590 tons nitrous vitriol of 60° B. and 11,395 tons chamber-acid of 50° B. Some of the sets have two or three parallel-acting towers, 17 to 21 feet high and 6 to 7½ ft. square; set No. V. has a tower 10 × 10 ft. square and 33 ft. high.

In some cases it is preferred not to fill the tower to its very top, viz. if the gas is thus cooled too much; for then part of the first-formed aqueous vapour might be condensed again to the liquid state, dilution thus counteracting the concentration. The temperature of the outgoing gas is generally about 60° C.; some manufacturers prefer from 60° to 75° C. But if too much cooling must be avoided by leaving the upper part of the tower empty, that portion might be left out altogether and the tower be made so much lower. In fact, towers from 18 to 20 feet high have recently been preferred to higher ones The height will, of course, depend upon the heat which the gas possesses when entering the tower, therefore upon the kind of ore burnt, upon the presence of dust-chambers, upon the length of way from the pyrites-burners to the tower, and so forth. According to numerous notes taken by me on this subject, the proper height for a Glover tower, under ordinary circumstances, seems to be from 20 to 25 feet. At one works, where two towers were erected, one 24 feet, the other 36 feet high, it was found that the higher tower did no more work than the lower, so that the expense caused by the additional height, both in erecting and packing, seems to have been useless.

The distribution of the acid for feeding the Glover tower is effected precisely as in the case of the Gay-Lussac tower, either by reaction-wheels (*suprà*, p. 593) or by stationary overflows (p. 595). Acid-wheels of different descriptions are shown in our first edition, pp. 438 to 440, and in the second edition, pp. 587 & 588.

For very large Glover towers it is preferable to employ several spouts, running right across the top of the tower, with a number of lips on either side, each connected with a pipe leading to a hydraulic lute on the top of the tower. The principle of this apparatus, which will be noticed in the Niedenführ tower, fig. 298, is the same as in the circular apparatus, figs. 257 to 259, which is adapted to towers of smaller sections.

The regulation of the flow for the Glover tower is nearly always effected by hand, or else by the apparatus shown on p. 601. Any apparatus for an absolutely constant supply of liquid would be out of place here, as the relative quantities of nitrous vitriol and chamber-acid vary, and must be regulated according to the state of concentration and denitration of the outflowing acid.

The cubic contents of the Glover tower worked by myself, and shown in our first and second editions, measured inside the lead without taking any account of the lining, the space underneath the dome, &c., for a daily consumption of 9 tons pyrites with 48 per cent. sulphur, amounted to 9 × 9 × 30 feet—that is, to 2430 cubic feet. This for every ton of sulphur burnt daily amounts to about 550 cubic feet; and this number may be considered the proper one for the proportions of a Glover tower; at some of the largest works it is closely approached. At the Saint-Gobain Company's works the real working-space (*i. e.* that occupied by the packing moistened with acid) is from 70 to 160 cubic feet per ton of pyrites, or, say, twice as much per ton of sulphur; and as the proportion of the working-space to the total space is not much more than 1 : 2, it may be said that the higher of the Saint-Gobain figures comes roundly to that which we have just stated as the normal one.

Description of complete Glover Towers.

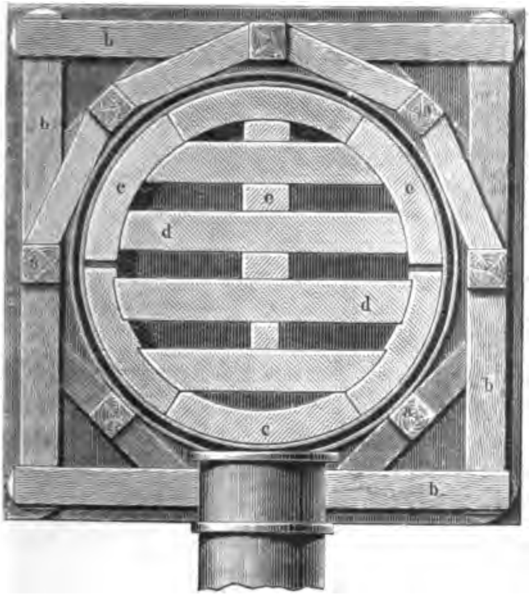
In the first and second editions of this book (2nd ed. p. 576 *et seq.*) I gave the working-drawings and detailed description of Glover towers such as were built from 1870 onwards, and as I had worked myself for a number of years. Many towers have been erected from those drawings, but I shall not repeat that description here, as it must be considered obsolete now, and I shall in place of this reproduce the designs of a modern Glover tower, as kindly supplied to me by Mr. Niedenführ, carried out in practice with fullest success at a considerable number of works.

First I shall notice some recent descriptions of Glover towers found in literature.

Instead of the square section at first universally employed for

Glover towers, latterly circular towers have come into use at many works. If lined with bricks, these are placed polygonally, unless suitable bricks, shaped to the proper bend, can be procured. In France the towers are usually lined with large blocks of Volvic lava, circular in section, and forming by themselves a substantial tower, although, of course, without any mortar, so that the lead shell is quite independent of them. Fig. 297 (from Frémy's 'Encyclopédie chimique,' t. v. section i. p. 188) gives a horizontal section of one of these circular towers which serves for a set of chambers of 160,000 feet capacity, and is constructed as follows:—It has a width of 6 ft. 9 in. and 23 feet height, and rests on a block of masonry, set in cement and protected on the top by an apron of 7 lb. lead. On this are erected eight uprights, *a a*, mortised into octagonal horizontal frames at top and bottom. The uprights are 10 or 12 inches square, and are connected by two rows of cross-pieces, *b b*, provided with iron binding-bolts. The holding-straps for the lead are attached to the uprights. The leaden shell consists of four drums which are burnt together in

Fig. 297.



their places. The first two are 11 millimetres thick (=25 lb. lead), the third 8 mill. (=18 lb.), the fourth 6 mill. (=14 lb.). This last drum is dressed inwards at the top edge, to be joined to the cover, which is suspended by means of straps from five railway-bars resting on the top frame. Until the lead drums are in their place, only five of the eight upright posts are put in, so as to leave a passage. Each drum is bevelled a little outward on the top edge, so as to form a seat for the next higher one ; the joint is then filled with molten lead. The drums, before fixing, are left on the wooden cylinder on which they have been made, and are hoisted and lowered down into their place with the cylinder still in. The lava lining is provided for the first three drums only; the fourth is left naked, as the gases are here sufficiently cool not to injure the lead. There are 18 pieces of lava, *c c*, six for each drum, in three courses with alternating joints, 10 or 12 inches thick; at Salindres they are 18 inches at the bottom, 12 inches in the middle, 8 inches at the top. The joints are made as thin as possible. The grate is formed by four or five sleepers made of lava, *d d*, as shown in the drawing; they are sometimes supported in the centre by a thin wall, *e*.

The advantage claimed for circular Glover towers is that they require less lead for a given cubic space and that the lead suffers less than when it is bent in sharp corners. But while for Gay-Lussac towers these reasons may be accepted, it is, in the case of Glover towers, doubtful whether they are not counterbalanced by the much greater trouble and expense of constructing the circular lining.

Benker (1902) has built circular Glover towers of Volvic lava with a leaden shell which have stood for twenty years and are likely to stand as many more; also towers without a leaden shell, which are cheaper and simpler to make, but about the durability of which nothing can be said up to now. The towers are placed on such high foundations that the pipe from the dust-chamber has a rise towards the tower, and can be easily cleaned out every month. The grate is also made of Volvic stone, frequently also the packing, which is employed in pieces up to the size of a child's head. These towers are never stopped up with mud.

Lüty gives a design of cylindrical Glover towers (Zsch. angew. Ch. 1896, p. 640) 10 feet wide. The bottom is protected by a double layer of acid-proof tiles, 8×8×3 inches. The sides are slabs. The tower is 8 ft. 2 in. wide and 23 ft. high within

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[*] A paper by Lüty & Niedenführ (Zsch. angew. Ch. 1902, p. 244 *et seq.*) g a reduced copy of these drawings.

lead (this suffices for a daily make of from 10 to 15 tons H_2SO_4). The lining commences with 15 inches brickwork From this springs a slotted arch, levelled at the top, where it has a thickness of 6 inches. This serves as support for six courses of very open brickwork, *m*, running in alternate directions (as shown in the drawings) and sufficing for the deposition of most of the flue-dust. The wide spaces between the bricks are not easily choked up, and, moreover, this part of the tower is accessible for cleaning, as it is covered by a second arch, *n*, running in the opposite direction to the lower arch. Thus the tower can from time to time be cleared out, by means of a short stoppage, without having to remove the whole of the packing, as is usually the case. On the second arch begins the proper packing, O, of Lunge-Niedenführ bricks, as shown in figs. 293 to 296 (p. 656), and here the lining soon diminishes to 10 inches. This packing occupies a vertical space of 8 feet, and is followed by a lining of 5 inches thickness, and 2 ft. 6 inches of packing, *p*, consisting of specially shaped dishes. The sectional plan at this level, fig. 299, shows the way these dishes or cylinders are superposed (similar to the Gay-Lussac, p. 589, fig. 252). The plan and sections of the top of the tower show the way in which the distribution of the acid is effected by means of the circular overflows *r*, lipped spouts *s*, and hydraulic lutes *t*.

As will be noticed, the dimensions and especially the working height of this Glover are much less than was formerly assumed to be necessary, and this means less cost. This has become possible through replacing the old, fortuitously acting packings of flints or quartz, and the much too open packing of cylinders, &c., by a rationally graduated and systematically acting kind of packing, modelled on the original principle of the Lunge-Rohrmann plates, but avoiding the conditions which make these plates unsuitable for Glover towers (p. 654), at least for the principal part thereof. The splendid results obtained with this packing at the six systems working at Oker (p. 657) are convincing proof of its efficiency.

At most works, quite properly, the Gay-Lussac and Glover towers are erected side by side, so that their tops are accessible by a common staircase, and even on the same level (in which case the Glover towers, being much lower, must stand on a higher foundation than the Gay-Lnssac towers). It is unnecessary to point out how much the supervision of the work, the feeding of the towers, &c. is simplified by this plan. The position of the Glover towers being given between the burners and the first chamber, it follows that the Gay-Lussac is at the greatest possible distance from the last chamber with which it is connected; but this is all the better, as the gases have more time to cool and get dried in the long connecting-pipe. It is also an advantage that the nitrous vitriol has not to run very far, as it sometimes contains gas (NO) which impedes its free running. As a long pipe increases the friction of the gaseous current, it mostly involves providing chimney-draught or else a fan-blast for the chambers, which is certainly the best plan for all reasons (p. 559).

Working of the Glover Tower.—The Glover tower may operate with only the nitrous vitriol itself running down in it, without any chamber-acid; but in that case it does not deprive the acid of all the nitrous compounds, but of the principal part only (down to about 0·2 per cent. of N_2O_3), and at the same time concentrates it to 152° Tw. This acid may now be used again in the Gay-Lussac tower for absorption; and thus a circulation of acid may take place between the two towers. There is in this process always a certain addition to the acid, as within the Glover tower itself, by the action of the sulphuric dioxide on the nitrosulphonic acid, free sulphuric acid is formed, as described on pp. 668 *et seq.*

However, the Glover tower is not usually fed (in the way just mentioned) with nitrous vitriol alone, except in the case of temporary disturbances. The apparatus is mostly so arranged as to be fed with nitrous vitriol (or with fresh nitric acid) and chamber-acid *together,* in which case not only is the denitration completed, owing to the initial dilution, but a very acceptable secondary effect is obtained, viz. concentrating the chamber-acid up to 152° Tw., and depriving it also of the minute proportion of nitre which it generally contains. If the acid is not, as is usual in England, brought in the chambers themselves to 116°–124°, but only to 106° Tw., it can still be concentrated to 144° without any difficulty in the Glover tower, even when the gas comes from a shelf-burner for pyrites-smalls and has therefore to be somewhat cooled in dust-chambers, on the supposition that the tower is placed close to the burners. That the denitration by sulphur dioxide becomes more perfect by dilution is a matter of course, according to the above-quoted researches of R. Weber, Cl. Winkler, and my own.

Where the leading-chamber is worked very strong, the Glover tower produces too strong an acid, which is incompletely denitrated and would injure the stability of the tower unless a little water is run down at the same time.

The stream of nitrous vitriol and that of chamber-acid are regulated entirely according to the degree of denitration and of concentration shown by the acid running off at the bottom of the Glover tower. The more chamber-acid is run through (that is to say, the greater the dilution), the easier will be a full denitration; the less chamber-acid is used, the more concentrated will the acid arrive below. There is, however, no difficulty in attaining *both* objects, viz. to get an acid at the same time completely denitrated and testing 152° Tw., if good pyrites be burnt, and if the burner-gas be employed as hot as possible, say 300° C. and upwards, by placing the tower close to the burners. In the case of poor ores or of smalls-burners with large dust-chambers, the denitrating action will also be complete; but the concentration cannot then be carried so far.

If it be assumed that the Gay-Lussac tower receives a quantity of acid equal to the total daily production, there will, of course, be just the same quantity of SO_4H_2 running down the Glover tower in the shape of chamber-acid, along with the nitrous vitriol, and therefore, according to bulk and weight, a little more of the chamber-acid, as this is more diluted. If the chamber-acid is on an average $=123°$ Tw., equal to 70 per cent. SO_4H_2, 117 parts by weight of the same correspond to 100 parts by weight of an acid of 152° Tw., $=81{\cdot}7$ per cent. SO_4H_2; or 100 vols. of the latter are equal to 128 vols. of the 123° acid, and the latter would be the proportion in which the two acids are mixed. The result would be a mixture of acids of 136° Tw. entering the Glover tower at the top, which can be fully denitrated by sulphur dioxide, especially when hot. If less Gay-Lussac acid has been used than the above, the mixture of acids entering the Glover tower will show a lower specific gravity than 136° Tw., and will be all the more easily denitrated.

During the first years of the working of the Glover tower it was generally assumed that the acids must only be mixed ***inside the tower***, because during their mixture nitric oxide would be given off. On this principle was founded the mixing-apparatus described by me in my first publication on the Glover tower (in Dingler's Journal, cci. p. 348), and the distributing-wheels with double outlet and separate distributing-chambers and pipes. But it follows from the calculation just made that a mixture of equal parts of acids, when chamber-acid of 123° Tw. is used and the daily make of acid is passed through the Gay-Lussac tower once a day, would be equal to 136° Tw. In an acid of this strength nitrososulphuric acid is sufficiently stable, at least at the ordinary temperature ; and it is possible, and has been done in many places for years past, to mix the two acids before they enter the Glover tower, which greatly simplifies the distributing-apparatus. Even when only one half of the total daily make of acid is used for absorbing, the mixture of this with the total chamber-acid still comes to 131° Tw., which is equally a safe strength. If, however, the conditions are more unfavourable in this respect, the dilution can no longer take place outside the tower. If, for instance, the chamber-acid is only 106° Tw. strong, 131 parts by weight of it correspond to 100 parts of acid of 152° ; and if of the latter only half the equivalent is taken (that is to say, 100 parts by weight of acid of 152° Tw. to 262 parts of 106°), the density of the mixture only comes to 118°, at which strength nitric oxide begins to escape from a solution pretty rich in nitrososulphuric acid ; but the above is an extreme case which rarely happens.

In these calculations the degree of saturation of the vitriol with nitrous compounds is not yet taken into account; the less the amount of acid used every day in the Gay-Lussac tower, the more will it be saturated with nitre, and there will be more danger of gas escaping from the nitrous vitriol when mixing it with chamber-acid.

The temperature of the acid running off from the Glover tower is usually between 120° and 130° C. (At Stolberg, in 1902, it was usually 120°, exceptionally up to 135°, the gases entering into the tower at 300°, sometimes up to 400°.) If the work is very much pushed, it may reach 140° or even 150°. In the few works where this happens, no bad consequences have been observed; but in one works I was told that a little more nitre was always used whenever the acid became hotter than 138° C. Still the observations made there were not sufficient to establish this result as certain, if all disturbing conditions be eliminated. The gas leaving the tower at the top has generally a temperature of from 50° to 80° C. (at Stolberg from 80° to 120°) ; it should not be above 60°, at which temperature cooling it before it enters the chambers is quite unnecessary.

One of Bode's towers, working with dust-burners, had to receive the burner-gas after passing through a large dust-chamber. The gas, therefore, only reached the tower 152° to 180° C. hot; and the temperature on leaving it varied between 30° and 40° C. The hot acid running off showed between 96° and 110° C. When this tower was only employed for concentrating chamber-acid, it daily evaporated 6 tons of water and produced 2 tons 3¼ cwt. acid of 144° Tw. from chamber-acid of 110°. This corresponds to a saving of coals for chamber-steam equal to 1½ cwt. per diem. When the tower was employed both for concentrating and denitrating, it supplied daily on a average 2 tons of acid of 144° Tw., and evaporated 9 cwt. of water; the denitration was perfect. The kiln-gas had 7½ per cent. by volume of sulphur dioxide. Of course the above results are much less favourable than with the usual initial temperature of 300° to 400° C. Even in the latter case the temperature of the gas leaving the tower does not exceed 50° to 60° C. Such a hotter tower of 8·28 square metres section, according to Vorster ('Dingler's Journal,' ccxiii. p. 411), in twenty-four hours evaporated 1400 kilog. water; another tower of 4·55 square metres section, 1048 kilog. water, the kiln-gas containing 8 per cent. by volume of sulphur dioxide.

Even when in Bode's Glover tower, by an accident, the percentage of the kiln-gas had sunk down to 6 or 5 per cent. of sulphur dioxide, there was still complete denitration and an evaporation of 7 cwt. of water daily, equal to 1·7 ton of acid of 144° Tw. Bode calculates from this that even when calcining the poorest ores the Glover tower still remains a useful apparatus.

Hasenclever reported as early as 1872 (Ber. d. deutsch. chem. Gesellsch. 1872, p. 506) that the Glover tower had been successful in combination with his plate-burners; I have found the same in combination with Malétra's or other shelf-burners in a large number of works, at all of which, of course, there were dust-chambers.

At those works where sulphuric acid is made from *brimstone*, Glover towers are not so regularly found as with pyrites-burners. The reason of this cannot be insufficient heat of the gases, as is proved by the practice of several large works where the Glover towers work perfectly well with brimstone-burners, and show all the advantages found elsewhere. Sometimes it is asserted that the higher value of brimstone acid as against pyrites acid is impaired by iron carried into it from the Glover tower; but this cannot take place except with an inferior description of packing material, and it is entirely avoided by confining the work of the tower to denitrating the nitrous vitriol, and taking the sale-acid from the chambers or from lead pans put over the burners. The real reason for the comparative neglect of the Glover tower at brimstone-acid works is this, that many of these works are of small extent and cheaply laid out, and are managed with insufficient care, so that their owners would rather lose nitre and sulphur than incur the expense of erecting and the trouble of working Glover towers. At several large American works I found Glover towers working most satisfactorily with brimstone-burners. In these cases the heat of the gases was first utilized for concentrating chamber-acid up to 140° Tw. or even (in H. Glover's sulphur-burner, *suprà*, p. 279) to 168° Tw., after which the gases entered the Glover tower and there produced acid of 150° Tw., with a temperature of from 126° to 130° C., sufficient in quantity for amply supplying the Gay-Lussac tower.

At larger works, possessing a number of Glover towers, it is a frequent and convenient arrangement to work them in different ways, viz., partly for making acid for the Gay-Lussac towers and partly for concentrating acid for the saltcake-pans. The first should be as strong as possible, and need not be entirely denitrated; it can be obtained in this state by feeding but little chamber-acid along with the nitrous vitriol. There is thus a constant interchange of acids between the two kinds of towers; but the Glover tower makes a good deal of fresh acid, so that part of it must at all events be employed for other purposes.

The acid for decomposing salt, or for sale, &c., on the other hand, should be entirely denitrated, and need not be so strong as the former; for this purpose much more chamber-acid is fed along with the nitrous vitriol.

We have already (p. 643) pointed out the *various functions* which are fulfilled by the Glover tower. The object for which it was first constructed, the *denitration of the nitrous vitriol*, that is the recovery of the "nitre" from this and the restoration of it to the chambers, is carried out by this means in the most perfect way and without any trouble. It is easy to work it so that the acid at the bottom contains even a slight excess of SO_2 (which is compatible with a very slight percentage of N_2O_3); nor is there any very high temperature required for it, especially when the nitrous vitriol is diluted with chamber-acid. In fact at some works the heat of the pyrites-kilns or the sulphur-burners is previously utilized for concentrating the acid, and the gases only then enter into the tower, where they perform the work of denitration, together with some little concentration, and are cooled down to the proper temperature for entering into the chambers. This plan is especially recommended for works where much acid is sold or is further concentrated to "rectified oil of vitriol," for which purpose the acid concentrated in the Glover tower is too impure (see below). This case also arises when burning arsenical ores, where the gases, in order to deposit the large quantity of flue-dust, have to pass very long channels (p. 390 *et seq.*).

That the fear of losing any nitre in the Glover tower by reduction to nitrous oxide or nitrogen is totally unfounded has been proved before (p. 639 *et seq.*). Far less nitre is consumed in the manufacture of sulphuric acid than before the introduction of the Glover tower; and the change has in most cases been so sudden that it seems impossible to overlook this evidence.

The second principal function of the Glover tower is that of *concentrating* chamber-acid, which is intimately connected with two other functions: *cooling the gases* and *supplying part of the steam* for the chambers. The concentrating action of the Glover tower was first studied in detail by Vorster ('Dingler's Journal,' ccxiii p. 413), but he neglects the acid brought over with the burner-gas as SO_3 and that formed within the tower itself. Both these sources have been taken into account in the investigation of Scheurer-Kestner (Bull. Soc. Chem. xliv. p. 98). From his analyses of burner-gases it appeared that these contained up to 9 parts of SO_3 to 100 SO_2; the average was about 3·5 parts. As there is enough water even in the air and the pyrites to hydrate the SO_3, it is sure to be retained in the Glover tower. He further shows the mistakes committed by Vorster in his calculations, from which the latter had concluded that very little acid was newly formed in the tower; and he opposes to this not merely the practical experience, according to which the introduction of a Glover tower saves from 10 to 20 per cent. of chamber-space, but also some special large-scale experiments made with an actual tower at the Thann acid-works, by carefully measuring for some weeks the excess of acid coming out from the tower over that going in. Thus it was found that the Glover towers made 15·7 to 16·3 per cent. of all the acid produced in the manufacturing apparatus. To this should be added the acid volatilized or mechanically carried away from the towers into the chambers, which was (only partially) estimated by measuring that which condensed in the connecting-pipes, and which amounted to 2 or 2½ per cent. of the total make, bringing the action of the towers to 17 or 19 per cent. This was entirely proved by the result of prolonged working on the large scale; for the same set of chambers which had previously made 6 tons of O.V. in 24 hours, made 7·28 tons, or 17·5 per cent. more, after adding a Glover tower to the apparatus.

Hence the concentration observed in the Glover tower is to a great extent only an apparent one; it is not merely due to volatilization of water, although this also takes place to a considerable extent, but also to the formation of very much H_2SO_4, which dissolves in the acid used for feeding and raises its strength.

In a previously quoted paper (Bull. de la Soc. Ind. de Mulhouse, 1889, p. 267; abstracted by me in Zeitschr. f. angew. Chem. 1889, p. 275) Sorel has tried to follow the functions of a Glover tower, so far as they refer to the new formation of sulphuric acid, by elaborate calculations. We must omit the greater part of these, as he at the outset commits several grave errors which modify some of his figures to the extent of four or five times the real values. This refers especially to Sorel's calculation of the number of times the nitrous gases enter into reaction during their passage through the Glover tower, and the time occupied by each such reaction; we shall, therefore, substitute for these a new calculation, based on the figures to be given later on, indicating the real quantities of nitre supplied to the tower in one shape or another at a well-managed works. We may assume that for each 100 parts of sulphur burnt in 24 hours there is in ordinary cases supplied to the chambers the equivalent of 10·25 parts of commercial nitrate, of which about $\frac{5}{7}=7·32$ parts are in the shape of nitrous vitriol, and $\frac{2}{7}=2·93$ parts in that of fresh nitric acid. These would yield the following quantities of oxygen for each ton, say 1000 kilog., of sulphur burnt; on being reduced to nitric oxide:

73·2 kil. 96 per cent. nitrate as

$$\text{nitrous vitriol yield } \frac{73·2 \times 8 \times 0·96}{85} = 6·61 \text{ kil. oxygen.}$$

$$\text{29·3 kil. ditto as nitric acid yield } \frac{29·3 \times 24 \times 9·6}{85} = 7·82 \quad \text{,,}$$

$$\text{Total } 14·43 \quad \text{,,}$$

Now each 16 parts of oxygen oxidize 32 parts of sulphur, entering the tower in the shape of SO_2, to H_2SO_4. Hence the above 14·43 kil. of nitric oxygen will produce sulphuric acid from 28·83 of sulphur, if its action is exerted only once. In reality, however, up to 250 of the total 1000 S are converted into H_2SO_4 within the tower, which certainly includes the SO_3 carried over from the kilns; but as this on an average does not exceed 3·5 per cent. of the total S, we shall be safe in assuming that 200 kil. S, as SO_2, are actually oxidized within the tower, so that $200-28{\cdot}8=171{\cdot}2$ kil. of S have been oxidized by renewed action of the nitrous gases. Considering further that the nitric acid is reduced to NO, and that in the further reactions this transfers upon SO_2 only as much oxygen as its equivalent of nitrous vitriol, the total oxygen transferable by each single action of the nitre present is only $6{\cdot}61+2{\cdot}21=8{\cdot}82$ kil., equivalent to forming sulphuric acid from 17·64 kil. sulphur. There must, hence, have been $\frac{171{\cdot}2}{17{\cdot}64}$, or, roundly speaking, *ten subsequent transfers of oxygen* upon SO_2 within the Glover tower after the first action of the nitre introduced.

We can also calculate the *time* occupied by each such transfer. The cubic contents of an ordinary Glover tower, counting the space within the lining from the surface of the grate to the top, varies from 180 to at most 300 cubic feet per ton of sulphur burnt in 24 hours. If we take the very usual capacity of 200 cubic feet, and deduct 50 per cent. for the packing (which is probably below the truth), and if we further assume that the denitration is practically complete halfway down the tower (which is decidedly allowable), we get $\frac{200}{4}=50$ cubic feet as the real empty space within which the acid-forming reactions take place, or slightly under 1·5 cubic metre. Now the volume of gases given off by the combustion of 1000 kil. of pyrites-sulphur in a properly conducted operation is, as shown on p. 400, about 8144 cubic metres, calculated for 0° and 760 millim. pressure. From this we must make a slight deduction for the gases taken out by the formation of H_2SO_4, say, up to the middle of the denitrating zone, equal to $\frac{1}{10}$ of the total $SO_2=70$ cubic metres, and the corresponding quantity of oxygen, equal to 35 cubic metres, leaving 8039 cubic metres at 0° and 760 millim. pressure, or, roundly 8000 cubic metres. As the average temperature of the denitrating zone is about 90° C., the above quantity of gases in reality occupies a space of about 10,700 cubic metres, or $\frac{10,700}{1\cdot5}=7107$ times the active space, that is the denitrating zone, of the Glover tower. Hence the sojourn of the gases within that space is $\frac{24\times60\times60}{7107}$, or as nearly as possible 12 seconds. But we have seen that there are eleven successive actions of the nitrous gases upon SO_2 within the tower, so that each of these, consisting, according to the older theories, of an oxidation and a reduction, or, according to the modern theory to be developed in the next Chapter, of the formation and decomposition of nitrososulphuric acid, cannot require much more time than one second.

We may draw another important inference from the established facts. The usual allowance of chamber-space per lb. of sulphur burnt in 24 hours is 20 cubic feet, or 44,800 cubic feet per ton of sulphur. Of this ton, one-fifth is oxidized into sulphuric acid in the Glover tower, leaving four-fifths for the chambers. This means that 50 cubic feet of active Glover-tower space, as defined above, make acid from 0·2 ton of sulphur, or 1 ton of sulphur requires 250 cubic feet, whilst 44,800 cubic feet of chamber-space make acid from 0·8 ton of sulphur, or 1 ton in this case requires 56,000 cubic feet. In other words: *the denitrating zone of the Glover tower makes 224 times more acid than an equal cube of chamber-space.* If we take the minimum chamber-space allowed at most English or German alkali-works, viz., 16 cubic feet per lb. of sulphur = 35,840 cubic feet per ton, this still means 44,800 cubic feet for the acid really made within the chambers, or only $\frac{1}{150}$ of the activity of the Glover tower *.

We shall now better understand why I recommend replacing a large portion of the chamber-space by columns acting in a similarly energetic way as Glover towers (pp. 478 *et seq.*).

This enormous action of the Glover tower is explicable on the assumption that the nitric oxide set free in the lower parts of the denitrating zone, according to the equation

$$2SO_5NH+SO_2+2H_2O=3SO_4H_2+2NO,$$

is fixed again in the upper parts by the reaction :

$$2NO+2SO_2+H_2O+3O=2SO_5NH\ ;$$

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* These calculations are more correct than those I have given in the Zeitschr. f. angew. Chem. 1889, p. 388, on the basis of Sorel's somewhat doubtful data and altogether wrong calculations.

the nitrososulphuric acid, thus re-formed, on descending into the lower regions is denitrated again, and the NO, thus flying backwards and forwards, incessantly and quickly transfers oxygen upon the sulphur dioxide arriving in the shape of burner-gas. This action, which, of course, equally takes place in the chambers, is in the Glover tower immensely aided by the continuous mixture of the gases and their constant shocks against surfaces wetted with nitrous vitriol. The very large amount of heat produced by the chemical reactions cannot give rise to any considerable elevation of temperature, as the heat is expended in evaporating water from the acid trickling down, and concentrating this acid, as already pointed out.

If the tower be too high, and if the top be kept too cool (which will depend upon the former), much less than the above calculated work will be done in it. In this case there will be a considerable condensation of the steam, generated below, in the upper region of the tower; this will facilitate the denitration near the top itself, and the NO here generated will be carried over into the chamber without performing the above-described multiple work. Experience has indeed long ago shown that Glover towers ought not to exceed a certain height (25 or at most 30 feet, comp. p. 657) to do the best possible work, both for evaporation and for forming new acid. But Sorel, in my opinion, goes very much too far in advising that the Glover towers should be kept as hot as possible, and should be fed with as concentrated an acid as possible. He looks at one side of the question only, and that decidedly the less important one, viz., that there should be as great a production of acid as possible within the Glover tower, by retaining the nitrous compounds within it a very long time. He neglects two other considerations of much greater importance: that by his mode of conducting the process the *denitrating* work is greatly impaired, so that the acid issuing at the bottom carries away very sensible quantities of nitre, and that by the great heat of the gases and the concentration of the acid the life of the tower is very much shortened. Sorel's plan interferes both with the complete denitration of the nitrous vitriol, and also with the important action of the Glover tower for bringing the chamber-acid just up to the strength required for decomposing salt, &c. (say, 140° to 145° Tw.), merely in order to force rather more SO_2 through the chambers than they can otherwise manage to oxidize; but this object does not seem worth incurring the serious drawbacks just mentioned.

The following *drawbacks* are connected with the Glover tower, the first of which is, however, only temporary, and much less felt where there is no coke-packing in the Glover, but only in the Gay-Lussac tower. This coke communicates to the acid, especially at the beginning, a brown colour (due to organic substances), which is quite immaterial to its technical application, but injures its sale. After a little time this ceases; and the acid running away from the Glover tower is then as clear as water, and, on account of its strong refraction of light and oily appearance, is compared by the workmen to "gin."

The contamination with iron is permanent, and is somewhat stronger than in acid made from the same pyrites in ordinary chambers, simply because the tower at the same time serves for keeping back the flue-dust. According to Hasenclever, his Glover-tower acid contained 0·05 per cent. of iron (Berl. Ber. 1872, p. 506).

Besides iron, the Glover-tower acid frequently contains considerable quantities of alumina, of course in proportion to the resistance of the lining and packing-material to the action of the acid and also of the arsenic.

The flue-dust and the sulphates of iron and alumina are often formed in such large quantities within the tower that it cannot be worked for any considerable time without being washed down occasionally by a strong jet of water. But in the long run this is not sufficient; the interstices get filled up with hard crusts, and the tower must be stopped for re-packing, which is a very troublesome and expensive operation. It is hence advisable to go to some extra expense for the best obtainable lining and packing-material.

An interesting application of the Glover tower is that for utilizing the nitrogen acids remaining in the acid from the manufacture of nitrobenzene and nitroglycerine; these are used in some works for running down in the Glover tower.

Where the Glover-tower acid is only used, apart from the service of the Gay-Lussac tower, for decomposing salt, for manufacturing manure, and for many other purposes, its impurities are of no consequence. But it cannot be used for such purposes where those impurities would be troublesome, and especially not for higher concentration to "rectified O.V." in glass or platinum retorts, as then hard adhering crusts of ferric sulphate are formed. Even then the use of a Glover tower need not be relinquished, but it must be either treated only as a denitrator, the heat of the burner-gases being *previously* utilized for concentrating acid (comp. pp. 274 & 310 and Chap. IX.), or else the acid required for the manufacture of rectified O.V. and similar purposes is taken out of the first chamber without passing it through the tower.

With Glover towers constructed on the Herreshoff system (that is, with quartz lining and quartz packing), there is no alumina in the Glover acid, but the iron and arsenic derived from the flue-dust still remain as impurities, so that there cannot be much difference as regards the crusts formed in platinum stills.

Denitration by other means.

The proposal of Garroway (E. P. 1673, of 1883) to effect the denitration and concentration of the acid without a Glover tower, by means of stoneware vessels placed in the gas-flue between the burners and the first chamber, seems to offer very little prospect of success.

Windus (E. P. 367, 1882) proposes, instead of denitrating the nitrous vitriol in Glover towers, to do this by agitating it within the chambers, and promoting the disengagement of the gases by producing a vacuum. The agitation is to be produced by mechanical means, or by allowing thin jets of acid to fall into the acid at the bottom of the chamber. It is unnecessary to point out the impossibility of denitration by this procedure.

CHAPTER VII.

THE CHAMBER-PROCESS.

Starting the Chambers.

In order to start a set of chambers, first of all the chamber-bottoms must be covered with acid. This is absolutely necessary when the sides are not burnt to the bottom, but hang loosely down into its upstand, as here an hydraulic seal is required to keep the gas within the chamber. Enough liquid for the sides just to dip into it is sufficient; for as the lead expands on the chamber getting warm, and as the liquid constantly increases by condensation, the hydraulic seal is constantly improving. However, for reasons to be stated hereafter, it is preferable to make the depth of acid as great as possible from the outset. Only in extreme cases ought *water* to be taken for luting the chamber; acid should rather be bought elsewhere at some expense to avoid this. If it can be done, the proper thing is to bring up the bottom-acid at once to at least about 90° Tw., better 100°. If this cannot be effected, this strength ought at least to be approached as nearly as possible. The reason why starting a chamber with water or very weak acid should be avoided is, that otherwise the vapour of nitric acid dissolves in the bottom-liquid and acts upon the lead.

Even if all the nitric acid freshly supplied were decomposed by sulphur dioxide before reaching the bottom, the presence of water or very dilute acid in large quantity would cause the new formation of large quantities of nitric acid from the lower oxides of nitrogen (N_2O_4, N_2O_3, and NO), and, on the other hand, of nitrous oxide, N_2O; there would thus be a great loss of nitre in both shapes, apart from the action of the lead, and the reactions within the chamber would be quite irregular. Altogether the chamber-process only goes on properly when there is an abundant quantity of pretty strong acid at the bottom of the chambers. If the sides are burnt to the bottom, it is even preferable to start a chamber dry to starting it with water; but otherwise a layer of about 4 inches of acid on the bottom of such chambers is preferred.

Supposing the chambers to be luted with acid, and the burners to be heated up so that they can be charged, the connection between them and the chambers is made and the burner-gas allowed to enter. Of course sufficient draught is given and nitric acid admitted at once, but at first no steam, in order not to dilute the bottom-acid too much. The nitric acid is introduced precisely in the same way as later on, either as vapour or in the liquid form. At first about three or four times as much is put in as is necessary afterwards, because there must be a stock of nitre-gas collected in the chambers, which subsequently needs only to be renewed so far as any loss is suffered. Liquid nitric acid can be introduced much more quickly than gaseous, since the latter depends upon the heat of the burner-gas working the nitre-oven; but with liquid acid the thing must not be overdone, since it might not be decomposed entirely before reaching the bottom. This can hardly happen when introducing it through the Glover tower. At the beginning from 12 to 15 parts of nitrate of soda, or a corresponding quantity of nitric acid, must be employed to 100 parts of sulphur; and this must be continued till the last chamber turns yellow; then the quantity is gradually diminished till the proper point is reached.

MacCulloch (Chem. News, xxvii. p. 136) prescribes starting chambers by admitting steam and nitre-gas from the steam-column (comp. p. 686) for five or six hours before the burner-gas is admitted. In that case, he says, the chambers work well from the first, and in one instance showed acid of 1·65 at the drips already in 12 hours. This may be so; but that process, while saving a little time and possibly a little nitre, from the outset detracts much from the durability of the chambers, since during the five or six hours when they receive only steam and nitre-gas very much nitric acid must condense, and whatever is gained by the drips is again lost by the previous dilution of the bottom-acid.

As soon as the drips and test-plugs prove that sulphuric acid is already forming in the chamber, steam is admitted, usually on the second day, but at first with great caution. Then all the factors of acid-making are at work, and the same rules are now valid as for the ordinary process. If every thing is in proper order, and if plenty of nitre is used (none of which, with a Gay-Lussac tower, is lost), a chamber may be in regular working order on the fourth, sometimes even on the third day after starting.

We must also take into account the opposite case, viz. *when a set of chambers has to be stopped for repairs.* It may be necessary to do so for one or two days, and it is, of course, most important to be able to go on again as quickly as possible, without losing too much nitre. If the proper precautions are neglected, it is possible that so much nitric acid is produced that the chamber-lead is seriously acted upon. To avoid this, we must proceed as follows:—First of all, the pyrites-burners are stopped; no fresh charge is put in, and all openings are closed as tightly as possible. Next to this the supply of nitre is stopped, but that of steam is continued, so long as the gas of the last chamber shows any outward pressure. When this has ceased, and there is on the contrary some inward suction, the outlet damper is closed, and air is allowed to enter at some lute, manhole, sight, &c., to avoid forcing in of the chamber-walls by the atmospheric pressure. Even now there is a good deal of acid produced, as proved by the action of the drips; but the steam should be shut off as soon as the drips go down to 100° Tw. When the drips cease to act all openings are shut. If the burners are started again within three days from the stoppage, it is only necessary to put on a good supply of nitre in order to get the chambers to work again; the regulation of the steam must, however, be as carefully attended to as when starting a new set of chambers.

Supply of Air.

The object of a regular chamber-process is of course this:—to make from a given quantity of brimstone or pyrites the greatest possible quantity of sulphuric acid with the smallest possible consumption of nitre. We may add at once, as less decisive, but still of importance, to make the chamber-acid as strong as is compatible with the two conditions just stated and with a saving of the chamber-lead. In order to attain that object, the attention of the chamber-manager must be directed to many points, some of which have already been treated of in detail, whilst others will be enlarged upon here.

1st. *Complete Combustion of the Sulphur-ore.*—This, with brimstone, follows as a matter of course; with pyrites it is much more difficult (compare also p. 314 *et seq.*).

2nd. *Proper Composition of the Burner-gas.*—This also has been treated of in the 4th Chapter; and we will here merely repeat that the proper composition of the burner-gas almost entirely depends upon the regular supply of air produced by proper regulation of the *draught*. We have already seen (p. 321) that, apart from chemical analysis, there are practical tests to show at the burners whether the draught is right or not. But at the chambers themselves this must equally be looked to, by means of the man-lids in the top, or the test-plugs (p. 508), or by pressure-gauges or anemometers (pp. 508 & 562). Generally, the following rules may be laid down as a rough guidance:—

In a set of three chambers the first chamber should show an outward pressure, and, accordingly, the gas should issue in force whenever a plug is opened. In the middle chamber the gas should be pretty nearly in equilibrium with the outer air; in any case there should be rather a little outward pressure than any inward suction. In the last chamber there may be some, but very little, inward suction; and behind it, but before the damper, the suction should be very perceptible. The Rhenania works (1902) keep some pressure throughout the chambers, diminishing gradually from front to back, the suction beginning only behind the Gay-Lussac, and this is also done at other well-managed works known to the author. Knapp compares the chambers to a lake traversed by a river: the speed of current at its inlet is diminished in the interior of the wide basin so as to be almost imperceptible; but at the outlet in the narrow draught-pipe it again comes out with the same strength as at first. Payen's 'Précis' (i. p. 318) states the speed of the gas within the chambers to be 8 to 10 inches per minute. Comp. also Niedenführ's measurements of pressures, p. 498.

Generally, it may be said that the draught must be sufficient to obtain a proper working of the burners and proper composition of the gas, but *no more than this*. The draught should be observed not merely by practical indications, but by testing the burner-gas for SO_2, and the exit-gas for O. The rule given can here be stated more precisely in this form:—There is so much draught given that the burner-gas from brimstone approaches a percentage of 11 per cent., that from pyrites 8 per cent. SO_2, as far as circumstances permit, and that the gas issuing at the end still contains 5 or 6 per cent. of oxygen.

A most important control of the working of the chambers, so far as the draught is concerned, is exercised by *testing the exit-gases for oxygen,* as has been described (p. 417), and will be mentioned later on in this Chapter. But there is no agreement on the question as to what is *the proper percentage of oxygen in chamber exit-gases.* Only so far there is general agreement that a certain excess of oxygen is required, over and above the theoretical quantity, in order to promote and hasten the regeneration of nitric oxide to nitrous acid, &c. Bode (' Beiträge,' p. 15) assumes as a minimum 6 per cent. of free oxygen in the exit-gas of the chambers, and mentions that at 8 per cent. free oxygen the yield had been quite as good as, and the consumption of nitre even a shade better than, at 6 per cent. According to Hasenclever (Hofmann's Report, i. p. 370), in 1866, before Schwarzenberg, Gerstenhöfer had already calculated the theoretically best composition of burner-gas, but had only communicated it privately to several factories. His figures, which do not materially differ from those quoted (pp. 397 & 399), are :—for brimstone,

10·65 per cent. by volume of SO_2,
10·35 „ „ „ O,
79·00 „ „ „ N;

for burning pyrites,

8·80 per cent. by volume of SO_2,
9·60 „ „ „ O,
81·60 „ „ „ N.

Scheurer-Kestner also assumes that the percentage of oxygen in the exit-gas=6 per cent. He has, however, proved that the oxygen in the *burner-gas* is considerably less than according to the above calculation, probably owing to the formation of SO_3 (p. 406).

The above is not universally accepted. Vogt contends (Dingl. Journ. ccx. p. 105) that there ought to be only 3 or 4, never above 5 per cent. oxygen in the escaping chamber-gas; beyond 5 per cent. he calls "very bad work." This opinion is shared by some, but not by many, other practical men. The other extreme is found at a large alkali-works, where it is believed that the best yield of sulphuric acid is obtained with 10 per cent. of oxygen in the exit-gas, certainly with a somewhat larger consumption of nitre than when 5 or 6 per cent. of oxygen is adhered to (4 per cent. of $NaNO_3$ upon the charge of sulphur, instead of 3 per cent.). The neighbouring works, burning the same pyrites under identical conditions, only allow 5 to 6 per cent. oxygen, and I think this decidedly right.

But if it is established that a certain excess of oxygen, although its presence increases the volume of gas, yet also increases the energy of the action in the chambers, it is, on the other hand, at least as well established that too great an excess of air vastly diminishes the yield and seriously increases the consumption of nitre. We here refer to the account of Olivier and Perret's first trials with pyrites (p. 325).

We may assume that in Germany the minimum and maximum of oxygen in the exit-gases is kept between 4 and 8 per cent. In France it is rather lower, say 3 or 4 per cent.; but in England the higher figure 7 or 8 per cent. seems to be preferred in many places. So far as my experience goes, a medium figure, 5 or 6 per cent. oxygen, would in the majority of cases be the proper one to aim at, but, if anything, I would rather allow a margin a little below than above that figure.

Excessive draught acts in a different way, according to whether the admission of air to the burners is regulated in the proper manner or not. If the action of the excess of draught extends to the burners, they will become too hot; sulphur will be sublimed, especially from brimstone-burners, but even from pyrites-burners, and in the latter scars will form. If, however, the excess of draught is *very* great, the burners may become cooled by the excess of air.

If the admission of air below the burner-grates is regulated so that these do not receive too much air, an excessive draught at the end of the system must produce a diminution of pressure in the chambers; air is aspirated through the tiniest chinks and crevices, and in very bad cases the sides of the chamber may be drawn in.

In both cases "false air" gets into the chamber, there is too much oxygen and inert gases, the chamber-space is badly utilized, and the excess of gases carries away both sulphur dioxide and nitrous gases. If the former is to be prevented by employing more nitre, too much work is put upon the Gay-Lussac tower and more nitre will be lost than in a regular way.

With *insufficient draught* at the end of the system there will be too much pressure in the chambers, as the hot gases continue to come over from the burners; after a short time there will be lack of air in these, which is shown by the analysis of the burner-gas and end-gas; the burner first becomes too hot, as the cooling effect of the air is missing, and scars are formed, whereupon they turn cold, the ore burns incompletely, and the gas gets poor. Generally this is accompanied by gas blowing out of the burners, which might, of course, also be caused by any kind of stoppage in the gas-flue, but cannot be confounded with this contingency, as in this case the pressure in the chambers is not too great, but the reverse. All this again leads to an excessive consumption of nitre, as the lower oxides of nitrogen do not meet with sufficient oxygen, and even NO may go away as such.

Either cause (as a consequence of the above) leads to a bad yield of vitriol, large consumption of nitre, escape of sulphurous acid into the air. Further proof is not required to show the importance of regulating the draught as accurately as possible.

In the case of poor ores, and those the sulphur of which is not readily given off, also in the case of burners admitting too much false air, such as the old Belgian burners, too much air gets into the chambers, and the yield is consequently always very bad. At Oker, for instance, in 1859, from a 50-per-cent. pyrites only 100 instead of 300 per cent. of strong acid was obtained, with a consumption of 14·4 parts of nitre to 100 sulphur (Knocke, in Wagner's Jahresb. 1859, p. 148); and the Belgian Commission states, for the four works examined, the yield=242, 237, 259, and 238 parts, instead of 306 as required by theory. They were able to detect in the escaping gas 0·38 to 1·26 per cent. of sulphur dioxide, and 11·7 to 17·4 per cent. of free oxygen.

The regulation of the draught takes place principally or sometimes even exclusively at the exit end by means of the contrivances described (p. 553 *et seq.*). It is not practicable to depend for this entirely on the ash-pit holes of the pyrites-burners (p. 321), as these must be regulated to suit each individual burner. It is very important not to overlook that the gas-pipe between the burners and the Glover tower and the chamber may be partially stopped up with deposit. In this case the draught at the burner will be bad, but will be little improved by opening the exit-damper ever so wide, and closing the latter will only draw in air at any chance crevice and injure the chamber-process. This cannot be overlooked if the process is properly controlled by regularly testing the burner-gas and exit-gas; if the latter shows enough or more than enough free oxygen while the burner-gas is blowing out, there must be some intermediate stoppage. The lutes or side-plugs, or still better pressure-gauges (p. 508) fixed in various parts of the set, will easily allow of localizing that stoppage.

On the contrary, some prefer working in this way, that there is always *ample* draught from the burners into the first chamber, by employing large and very loosely-packed Glover towers; the burners in this case never blow out, and yet the chambers themselves can be worked right to the end, with even outward pressure in lieu of inward draught. But there must then be this drawback that, owing to the loose packing, the denitration in the Glover tower will be hardly perfect. This can be obviated by the following plan, which may be usefully adopted in special cases:—The Glover tower is packed as usual, so as to be an efficient denitrator and concentrator. From it the gases are still made to ascend a sufficient height, say 6 or 10 feet, in a wide tube, which then turns (avoiding any sharp bends) sideways and dips down into the roof of the first chamber. Thus a siphon is formed, and as the gases in the second, descending limb are cooler than in the part rising upwards from the tower (in extreme cases the air-cooling might even be supplemented in summer by water-cooling), this will cause suction of the gases from the tower, and thus increase the draught from the burners, without drawing the gas away from the chambers too quickly at the other end. Of course this result is much more easily attained by a fan-blast (p. 559).

Exceptionally, air is admitted behind the burners, usually by means of an injector in the first chamber which is so constructed as to introduce some air along with the steam (p. 553). This must be done where the burner-gases are too rich, and especially where the first supply of air is purposely kept as low as possible, in order to get hotter gas, as, for instance, in H. Glover's brimstone-burner (p. 279), which is intended to concentrate the acid by the heat of the gases.

Some chamber-managers contend that no regulation of the draught need take place at the outlet when this has been done once for all, as the outside atmospheric conditions are never so varying as to interfere with the working of the process. But this opinion is decidedly wrong. In most parts of Central Europe the temperature may vary up to 40° C., or even more, between the extreme heat of summer and the extreme cold of winter. But this means that for every 1000 cubic feet of air required in the coldest season, nearly 1150 cubic feet must pass through the apparatus in the hottest season, supposing the barometric pressures to be equal. But these latter as well may vary 30 millimetres, or even more; so that, for instance, 1000 cubic feet at 760 mm. pressure represent the same weight of air as 1041 cubic feet at 730 mm. Combining both (and very frequently low temperatures and high barometric pressure go together, as well as high temperatures and a low barometer), 1000 cubic feet in winter may be equal in weight to 1200 cubic feet in summer. It is quite evident that such large differences, and even much lesser ones, as they may occur from day to day, *must* be compensated by regulating the outlet of the gases accordingly. Nor must it be overlooked that the pressure of wind affects the quantity of gases passing through a given orifice, and this circumstance sometimes during the year has a very serious effect on the draught, even when the burner-house (as it ought to be) is sheltered against the direct action of gusts on the ash-pits.

The great lack of *quantitative* statements as to the draught necessary in various parts of the chamber-system has been partially remedied by an investigation by Nörrenberg (Chem. Ind. 1899, p. 48; comp. also the criticism by Eichhorn, ibid. p. 150, and Nörrenberg's answer, p. 237). The required pressure within the chambers can be attained only by a strong up-draught. To produce this, we should make the difference of level between the burners and the Glover tower as great as possible. The gas inlet-pipe from the burners to the Glover tower should rise straight up, and should deliver the gases into the tower at the highest practicable temperature. The temperature of the gases leaving the Glover tower should be very little above that of the main chamber, and any gas to be carried downwards should be cooled as much as possible. The gas leaving the last chamber may descend pretty low towards the Gay-Lussac, which (of course!) gives all the better draught the greater its height and the wider the outlet. The loss of up-draught from the burners should be lessened by giving the connecting-pipes and flues a sufficiently large section for producing the following velocities (having regard to the greatest possible production with normal burner-gases, to the temperature ordinarily attained at the respective places, and the inequalities of work):—

About	0·5	metre	per second	in the	(clean) burner-flues.
„	1·0	„	„	„	Glover inlet-pipe.
„	0·8 to 1	„	„	„	Glover grate.
„	0·25 to 0·5 (if possible rather less)	„	„	„	Glover packing.
„	1·0	metre	per second	„	connecting-pipe leading to the last chamber.

The velocity in the pipe leading to the Gay-Lussac and that in the outlet-pipe of the latter should be such that, on deducting all the losses of pressure up to the Gay-Lussac outlet from the effective up-draught there remains a pressure of 2 mm. water at the Gay-Lussac outlet at ordinary temperatures. This is advisable, in order to facilitate the regulation of the final damper. The section of the Gay-Lussac should be equal to that of the Glover tower, or a little less. It should not be made proportional to the quantity of gas at the respective temperatures, on account of the coke packing. Changes of velocity, curves (especially with a small radius), and elbows should be avoided as much as possible. By rounding-off the edges in the chamber-exits the loss of pressure can be practically avoided.

Hasenclever (Chem. Ind. 1899, p. 27) found in a special case that a Glover tower with good draught showed a pressure of 2 mm. water at bottom and 5 mm. at top; when the pressure was 2 mm. at bottom and 2·5 mm. at top, the tower was found to be obstructed. But he justly points out that no definite figures for the pressure in the various parts of the chamber-apparatus can be stated as a general rule, and that they must be fixed by experience for every special case.

In *horizontal* ducts the loss of pressure can be deduced from the mere observation of the pressure-gauge, but we shall quote a very important remark made to Hasenclever by Dr. Drecker, concerning the complication caused by the *difference of level* through the difference of barometric pressure at different heights of the apparatus, neglect of which makes any observations of pressure by a manometer quite unintelligible. Taking the just-quoted example of a Glover tower, showing 2 mm. water-pressure at bottom and 5 mm. at top, but possessing a height of 9·5 metres (about 31 feet), the difference of atmospheric pressure between the bottom and top of the tower at 15° C. and 750 mm. mercurial pressure in the barometer is :—

$$\frac{1{\cdot}294}{1+\frac{15}{273}} \times \frac{750}{760} \times 9{\cdot}5 = 11{\cdot}5 \text{ mm. water.}$$

This we must introduce into our formula, and we thus obtain:

$$11{\cdot}5-(5-2)=8{\cdot}5 \text{ mm.}$$

as the real difference of inward pressure in the tower; that is to say, the pressure within the tower is =8·5 mm. water higher at the bottom than at the top, and this difference has on the one side to carry the weight of the gaseous column, on the other side to procure the movement of the gases. Taking the specific gravity of the gases =1·374, and the mean temperature within the tower (350° at bottom, 95° at top)=222° C., and the outward pressure =750 mm. mercury, we find :

$$\frac{1{\cdot}374}{1+\frac{1}{273}\times 222} \times \frac{750}{760} \times 9{\cdot}5 = 7{\cdot}10 \text{ mm. water;}$$

or a pressure of 7·10 kil. per square metre. The difference 8·5−7·10=1·40 indicates the pressure, in terms of millimetres of water-pressure, which causes the ascending movement of the gases.

If we call the difference of weight between a gaseous column and a column of air of equal height its *upward stress* or *buoyancy*, in the present case 11·5−7·10=4·40, we find the *loss of pressnre* between two points in the system to be equal to the observed manometric difference of pressure *plus* the buoyancy; in the present case: observed manometric difference (−3) + buoyancy (+4·40) = 1·40 *loss of pressure, in that special Glover tower*, caused by frictional resistance between its bottom and top, &c. If the tower were obstructed by deposits, this loss of pressure would become greater, and we can by similar calculations establish *for any given apparatus* and *by special observations* the best conditions to be aimed at, but we should commit a great mistake if we attempted to lay down a *general* rule for all cases from such special observations.

In this case, as well as in well-nigh every other case in chemical manufacturing, it is entirely premature to apply apparently exact mathematical formulæ as a general guide for actual practice, as Sorel has done by applying to vitriol-chambers Clegg's formulæ for the movement of gases in pipes. The extraordinary complication of the case, caused by the sudden expansion of pipes into the enormously larger section of chambers, by the sharp angles through which the gases must sometimes be conducted, by the changes of temperature, and by the chemical reactions which cause alterations in the volume of the gases and vapours, &c. &c., make the application of any simple formula quite illusory. These formulæ may overawe those who are ignorant of mathematics, especially when they contain the (for such people) mystic symbols of higher mathematics, but I know absolutely of no case in the whole range of manufacturing chemistry where the least practical progress has been made by applying complicated mathematical formulæ to chemical operations. The time for this may come in the (probably somewhat distant) future, when the *elements* necessary for such calculations have been thoroughly studied and placed on a secure *experimental* basis.

Supply of Water (Steam).

The regulation of the steam or water-spray is one of the most important parts of chamber-management, and should always be taken in hand by the responsible foreman or superintendent himself. One of the first conditions for enabling him to do so properly is that the tension of the steam should be kept as nearly equal as possible; and it is hardly necessary to point out how much this task is facilitated by a registering steam-gauge or by automatically regulating steam-valves (pp. 531, 533). The round of the chambers should be made two or three times a day; at some works it is even made every other hour. It is one of the advantages of the water-spray system (p. 536 *et seq.*) that there are hardly any variations of the quantity of water supplied, but other difficulties may occur instead (p. 538).

It must be borne in mind that the Glover tower supplies the first or "leading" chamber of a set with a good deal of the steam required. Hence steam or water-spray must be supplied to this chamber in much less quantity than when working without a Glover tower, and the position of the jets is also influenced by this (comp. p. 534).

A rough indication, whether too little or too much steam is present, is sometimes sought in the appearance of the glass jars covering the top lutes of the chambers (p. 508). If these show a white crystalline covering of chamber-crystals, which are proved as such by turning green on moistening them, there is evidently a deficiency of steam. If, on the other hand, the glass jars are dripping wet, there is too much steam in the chamber. This is, of course, only to be taken in conjunction with the other observations to be made by the attendant.

The proper indicator for the admission of steam or water is the *strength of acid made in the chamber*, both as observed in the acid-drips (p. 506) and in the bottom acid. These two are never identical; the drip-acid is always more or less strong than the bottom acid. In long chambers there is a considerable difference between the front and the back part, and such chambers should be provided with two or even more different sets of drips.

Considerable difference of opinion exists as to the strength of acid most conducive to a proper working of the vitriol-chambers—that is, to the best yield, the greatest production for a given chamber-space, and the smallest consumption of nitre. We may say generally that the chamber-acid is kept much stronger in the majority of English works than in the majority of Continental works. Whilst the former mostly keep the acid in the leading chamber from 120° to 130° and the drips often 5 to 10 degrees higher, the usual practice on the Continent is to keep it at 106° to 110°, or at most 116° Tw. At the Rhenania works the acid runs away from 106° to at most 116° Tw. In America I found from 112 to 116 degrees. Only exceptionally higher strengths (up to 124° Tw.) are met with on the Continent or in America.

It is unnecessary to say that both English and Continental manufacturers firmly believe that they are in the right, the former in making stronger, the latter in making weaker chamber-acid. Both contend that in their, and only in their way the best results are obtained. It is difficult, if not impossible, to arrive at any certain decision on the question from a comparison of the data supplied by various works as to the strength of acid, the yields, the consumption of nitre, the chamber-spaces, and so forth. This difficulty arises both from the complication of the various conditions, which interact upon one another, and from the very frequent inaccuracy and incompleteness of the obtainable figures. It is therefore with all reserve that I proceed to give my own opinion on this question (which differs from that given in the first edition of this work, vol. i. p. 346).

All *theories* of the vitriol-chamber process seem to point to the preference of the *weaker* rather than of the stronger acid. Hurter, in his dynamical theory (J. Soc. Chem. Ind. 1882, p. 10) arrives at the result that the chamber-space is inversely proportional to the quantity of nitrogen compounds present, and to the amount of water present in the gaseous condition; in other words, that, other conditions being equal, the quantity of acid produced within a given chamber-space is larger when weaker acid is made than when strong acid is made. It is true that the evidence given for this in the paper just mentioned from the actual results of a number of chambers is very scanty, and certainly not sufficiently conclusive in itself; this was unavoidable, as only such works could be quoted which did not possess Gay-Lussac and Glover towers. But, at all events, no contrary assertion can be based on that evidence.

The theory propounded by myself, and the very similar one of Sorel, both of which will be found at the close of this Chapter, also demand that, other conditions being equal, the sulphuric-acid forming reaction is promoted by a larger amount of water, up to the limit where an excess of water would produce other, injurious, reactions.

Another point to be considered is this, that it is practically impossible to prevent the loss of some nitre, dissolved in the chamber-acid as nitrososulphuric acid, but that the tendency of the chamber-acid to retain nitre in this form rapidly increases with its strength. Theory would therefore demand keeping the acid weaker in order to lose less nitre. Whether this is so or not in practice can only be proved by bringing together a great many *reliable* data, the difficulty of doing which has been pointed out before. It is a *fact* that sometimes "pale" chambers are the consequence of giving too little steam (that is, keeping the acid too concentrated), and that this evil can be remedied by turning on full steam for a short time, when the chamber will become red again.

The practice of most Continental factories, including several German and Austrian works, at which all the processes are followed up in the laboratory with the greatest care, and which are generally admitted to work with the greatest perfection, is in accordance with the just-quoted theories, and comes to this: that the acid in the leading chamber, that is at the same time that which is withdrawn from the process for use or sale, should not exceed 113°, and is best kept at from 106° to 110° Twaddell. Thus the best yield and the smallest consumption of nitre are attained.

The usual and practically the only reasonable motive of English manufacturers for making their chamber-acid so much stronger is, of course, this, that they save the expense and trouble of concentrating the acid for use or sale. But there is little or nothing in this in the great majority of cases. For the manufacture of superphosphates, which requires an enormous quantity of sulphuric acid, and for which many acid-works are exclusively employed, the strength of 110° Tw. is quite sufficient. For decomposing salt for sale and for making rectified oil of vitriol a higher strength is certainly required. But at every works provided with Glover towers (that is, at every properly equipped works and actually in the great majority of existing factories) there is no difficulty whatever in bringing all the acid up to 140° Tw. without any expense, even when starting from chamber-acid at 110° Tw.; and this is done even without Glover towers (for further concentration in platinum stills) at many works by means of the waste heat of the pyrites-kilns.

. Some years ago, P. W. Hofmann (Ber. d. deutsch. chem. Ges. iii. p. 5), starting from the (erroneous) assumption that sulphurous acid in contact with nitric acid and sulphuric acid of, say, 100° Tw., produced much nitrous oxide, N_2O, proposed to diminish the steam in the first chamber (which in his case was only a "tambour" of 3500 cubic feet capacity) to such an extent that acid of 140° Tw. should be formed; in this way the acid dissolves much nitre, and is run into the following large chamber, where it gets diluted and gives up the nitre. He asserted that he had thus effected a saving of 1 lb. nitre on 100 lbs. of sulphur; but as his original consumption of nitre and the yield are not stated, and as, moreover, his chambers had no Gay-Lussac and Glover towers, that alleged saving cannot convey any proof of the utility of his proposal, upon which a vigorous controversy was carried on in the 21st volume of the 'Chemical News' (pp. 132, 164, 189, 200, 224). It was then mostly overlooked that Hofmann's small "tambour" of 3500 cubic feet capacity had very little in common with an ordinary English leading chamber of more than ten times that capacity. Apart from all other reasons, the undoubtedly much greater wear and tear of the chamber, when worked in the described way, would tell much less with a small "tambour" than with a large chamber. But, for the reasons above stated, Hofmann's process seems wrong in principle, and has not met with any success whatever on the Continent, where it was first tried.

In England later on (since 1889), probably without any reference to Hofmann's proposal of 1867, several works in Lancashire began to employ much stronger acid in the leading chamber, up to 140° Tw. It is, of course, out of the question to lose the nitre dissolved in such strong acid; none of it must be used without first passing through the Glover tower, and as it would become too strong therein, and would be incompletely denitrated, a little water is run through the tower at the same time. At one of the works visited by me it was stated that, with the very low chamber-space of 17 cubic feet per lb. of sulphur, the excellent yield of 41½ cwt. of 96 per cent. salt-cake was obtained per ton of pyrites, with the very small consumption of 15 lbs. nitre per ton of pyrites (=0·67 per cent.). These good results were ascribed, firstly, to an extraordinary large Gay-Lussac space; secondly, to the above procedure, by which an unusually large quantity of nitre was supposed to be kept circulating in the vitriol-chamber. It was not denied that there was more wear and tear of the chambers; but it was believed that this was no more than would be compensated by the saving in the process.

At the time of my visit to the above and a few other works, where the same method was followed, the process had not been sufficiently long in use to enable a correct judgment to be formed as to the yield and the consumption of nitre. Everybody knows that it requires many months to make sure of this, and to avoid any accidental gains and losses. But even taking it for granted that the above-quoted excellent results were really confirmed in the long run, I am very strongly disposed to place these results rather to the credit of the colossal Gay-Lussac towers, of a width of 14 feet and a height of 60 feet, than to that of keeping the chamber-acid at the dangerous strength of 140° Tw. It is clear that the large quantity of nitre kept in solution in the strong acid of the leading chamber can contribute but very little to the work of oxidizing sulphurous into sulphuric acid; its work can be done only whilst running down the Glover tower. But then the same object can be attained quite as well, while keeping the chamber-acid at a lower strength, by supplying the Glover tower with more nitre, either (once for all) in the shape of nitric acid, or (continuously afterwards) in that of nitrous vitriol from the Gay-Lussac tower; the inert stock of nitre at the bottom of the leading chamber is thus very largely reduced, and the confessedly much greater wear and tear of this chamber and of the Glover tower is thus avoided. From all indications it is also likely that less chamber-space will be required in this than in the former case.

It is difficult to say anything general as to the strength at which the *drips of the first chamber* ought to be kept. At one works the drip-acid is only 2 or 3 degrees, at others 15 degrees or more above the bottom-acid; at others it is always weaker than the bottom-acid. Everything depends on the position of the drips; but so much is certain, that in the same plant the difference between the strength of the drip-acid and that of the bottom-acid is nearly constant, and that the attendant must manage his chambers accordingly. On the average, the drips where they are taken from the inside, clear of the chamber-sides, show about 10° Tw. more than the bottom-acid; but this holds good only with the ordinary style of working, not with that described above, where the bottom-acid is kept at 140° Tw.; in this case the drips are not very much or not at all stronger; and where the drips are collected at the chamber-sides they are generally somewhat weaker than the bottom-acid.

We have seen above (p. 195) that the tension of aqueous vapour varies both with the temperature and with the strength of the acid; for instance, at 80° (near the chamber-side), acid of 114° Tw. has exactly the same vapour-tension as, at 95° (only 2½ inches within), acid of 128½° Tw. Sorel observed that the acids collected at various points of the same transverse section of the chamber really showed such differences of strength, and that, therefore, it may be said that they are all at an equilibrium of aqueous-vapour tension. This shows how useless it is to compare the drips of different sets of chambers, unless they are fixed in a precisely similar position to one another.

The strength of acid in the intermediate chambers, between the first and the back chamber, is always below that of the first chamber. The second chamber, in a set of three, has generally about 10° Tw. less than the first; but with acid of 140° Tw. in the first chamber the difference between this and the second may amount to twice as much. In a set of four or more chambers the strengths will naturally diminish more gradually.

The *last or "back" chamber* is kept at very different strengths, according to whether there is a Gay-Lussac tower connected with it or not. In the latter case the acid is never kept above 75°, and sometimes as low as 50° Tw., or even less than that. It is, in fact, difficult to keep the strengths higher, as there is so little sulphur dioxide present, and as there must not be a large quantity of nitre, in order to avoid losing an enormous proportion of it. Thus there is but little acid made here, and it is correspondingly weak. But such weak acid, even at 75°, causes the formation of much nitric acid, which must act on the chamber-lead and is otherwise injurious. Hence with the old style of working without nitre-recovery apparatus, the last chamber was always a very weak link of the set.

In the presence of a Gay-Lussac tower there is no reason whatever for keeping the last chamber below 90° Tw., or even a few degrees above this. There will be no formation of nitric acid to be apprehended in this case, and the gases will be better dried in preparation for the Gay-Lussac tower. The practice of some works to go down as low as 75° or 80° Tw. in the back chamber cannot be at all recommended.

Crowder (J. Soc. Chem. Ind. 1891, p. 301) prefers placing the "drips" in the connecting-pipes between the chambers, and keeps them as nearly as possible at the following strengths:—drip from Glover tower to 1st chamber = 95° to 105°; from 1st to 2nd chamber = 130°; from 2nd to 3rd chamber = 122°; from 3rd to 4th chamber = 105°; from 4th to Gay-Lussac = 85°. If the drip from No. 1 to No. 2 chamber stands lower than 130°, the consumption of nitre is increased. [The drips in the connecting-pipes do not correctly indicate the work done in the chamber, as in consequence of the far greater cooling-action the formation of acid in these places must be abnormally large.]

Sorel gives the following directions for the strength of acid to be observed in a set of three chambers (degrees Baumé) :—

	Inside drips.	Side drips.	Acid in chamber bottom.
1st chamber	57-85° B. up to the middle. 56 second half.	51–54°	54·5–55°
2nd chamber	52–53°	42–43° first half. 45–47° 2nd ,,	48 –48°·5
3rd chamber	52–53°	45–50°	48·0–84°·5

We shall now describe *the injurious results of a wrong supply of water* (as steam or spray) to the chambers.

The first and most obvious result of giving *too much steam* is this, that the acid gets too weak. But this is a minor affair compared with what immediately follows. If the lower oxides of nitrogen meet with an excess of oxygen (which is always present in the chambers) *and at the same time with an excess of water*, the following reactions take place:—

$$2NO+3O+H_2O=2NO_3H;$$
$$N_2O_3+2O+H_2O=2NO_3H.$$

That is to say, they are converted into nitric acid, which, in the first instance, is a much less efficient carrier of oxygen than nitrous acid, and, secondly, is to a great extent dissolved in the bottom-acid; here it assists the acid-forming process very little and, moreover, acts, upon the lead. So long as the botton-acid is pretty strong (say, up to 90°), it will not long keep the nitric acid, but again give it off as lower nitrogen oxides by the action of sulphur dioxide; but if the excessive supply of steam continues, it will soon keep the nitric acid back; and as the process is thereby disturbed, even the steam* which should have been used up in the formation of sulphuric acid is condensed to water, and the dilution of the bottom-acid thus again increased. If this state has once set in, it is not always easily remedied. Cutting off the steam is not sufficient; much more nitre must be put in as well; and yet the bottom-acid only gradually gets up to its normal strength. In the meantime the yield falls off, the consumption of nitre increases very much, and the action on the chamber-lead does permanent damage. Thus it is apparent that an excess of steam does very much harm; and great care must be taken lest the strength of the acid should go down below the proper amount. The chambers soon show when they have too much steam by becoming pale. A pale chamber often gets red again in an hour after the supply of steam has been partially cut off.

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* Whenever here, and in other places, we speak of "steam" in connection with the supply of chambers, water in the shape of spray or mist is also meant; it would be tedious to mention this in every instance.

An excess of steam has another injurious effect, which can only be explained in detail when treating of the theory of the chamber-process, viz. the formation of nitrous oxide, or even of nitrogen, whilst the reduction of the nitrogen-acids ought not to go beyond nitric oxide. Neither nitrous oxide nor nitrogen can be reoxidized to nitrogen-acids; but they escape with the other gas, and thus cause a loss of nitre.

We will now consider the opposite case, viz. that *the chambers receive too little steam.* According to the theory of the vitriol-chamber process, to be developed later on, this must deteriorate the conditions for the formation of sulphuric acid, since the substance formed in an intermediate state, viz. nitrososulphuric acid, cannot then be entirely decomposed into sulphuric acid and nitrous acid. It will in this case be either separated in the solid state, as "chamber-crystals," or else it will dissolve in the bottom-acid. In actual practice it rarely happens that the deficiency of water is so great as to lead to the occurrence of solid chamber-crystals within the chambers; more frequently this happens in the connecting-pipes. But it is all the more general, nay unavoidable, that some chamber-crystals (commonly called "nitre" in this case) dissolve in the bottom-acid. We shall see later on that a certain quantity of "nitre" *must* be present in properly working chambers; but if there is too little steam, this quantity will be largely increased, both by a deficiency of water in the acid mist floating about, which leaves a large quantity of nitrososulphuric acid undecomposed, and by the excessive concentration of the bottom acid, which enables it to hold more "nitre" in solution. Thus the nitre will be removed from its proper sphere of action, the atmosphere of the chamber, and SO_2 will escape oxidation. Where the chamber-acid is directly used, without first passing it through the Glover tower, this nitre will be finally lost. All this, of course, happens less easily where the bottom-acid is kept at a lower strength, as on the Continent; there is in this case more time for repairing a temporary deficiency of steam as indicated by testing the drips and bottom-acids for strength and nitre.

A deficiency of steam also acts in this way, that the acid becoming too concentrated, may to some extent act upon the lead. So long as the strength of the chamber-acid does not exceed 144° Tw. (and this will very rarely happen, even with faulty management), the harm is not much. For very good reasons, the last chamber, if a Gay-Lussac tower is present, receives very little steam, in the case of smaller chambers (tambours) none at all. But this may be carried too far; and then, in spite of the dark-red appearance of the chambers, there is a bad yield of acid, because the water necessary for its formation is missing, and SO_2 and O go away uncombined. This occurs especially when the chamber appears of a very clear, transparent red, instead of being somewhat dim and misty.

On the whole, it is evident that the risks run by a deficiency of steam are nothing like so serious as those arising from an excess of steam.

Hurter ('The Manufacture of Sulphuric Acid,' Liverpool, 1882, p. 16) gives the following rules for utilizing the indication of the chamber-drips:—

1st. If the strength of the acid in the drips is *correct* but deficient in quantity, the chamber is short of nitre.

2nd. If the strength is *high* and quantity not far short, the chamber is very rich in nitre; but if the quantity is short, it has too little steam.

3rd. If the strength is *low*, but the quantity full up, the chamber has too much steam. If, on the other hand, the strength is low and the quantity short, the chamber is very poor in nitre.

It is needless to say that the indications afforded by these rules would be sometimes very misleading, the conditions being too complicated, if they were not supplemented by direct observations of the amount of "nitre," the temperature, and the composition of the inlet- and outlet-gases, as shown below.

Supply of Nitre.

It is quite evident that those ingredients from which sulphuric acid is ultimately formed, namely sulphur dioxide, atmospheric oxygen, and water, must be supplied to the chambers in proportions varying within very narrow limits only, as any undue excess or deficiency of one of these will cause a corresponding waste. Sulphur dioxide being considered as the given quantity, the proportion of water supplied is kept so that a very nearly constant concentration of the chamber-acid is obtained; and in like manner the supply of air is regulated by the draught in such a way that a certain necessary excess of oxygen, but no more than this, is found in the exit-gas. But the matter is different with that reagent which does not enter into the composition of the ultimate product, and only serves as an intermediary agent for combining SO_2, O, and H_2O, without (in theory) suffering any real change or loss at the end of the process. We now call such an agent a *catalyzer* (see later on): this is, of course, the "nitre," by which expression we understand all the compounds of nitrogen which are concerned in the manufacture of sulphuric acid, at whatever stage of oxidation or combination they may exist at a certain moment.

It is almost self-evident that the acid-making process can be made more or less rapid by supplying more or less nitre, and that this finds expression in the greater or smaller space which the process requires. In fact considerable variations may be made in the supply of nitre, according to whether the chamber-space is to be utilized as fully as possible or not, and up to a certain extent it may be said that the supply of nitre must change in an inverse proportion to the chamber-space present. But certain limits do exist here as well, both in an upper and in a lower direction. If there is too small a supply of nitre, the reactions become too sluggish and very disastrous consequences follow, which cannot be avoided by any amount of chamber-space; and if too much nitre is supplied, the temperature rises too much, the chamber-lead is acted upon, and part of the nitre escapes the process of recovery. We shall refer to this subject in detail later on.

The *supply of nitre* must be regulated on entirely different principles, according to whether there is an apparatus for the recovery of nitre or not. In the latter case care must be taken not to have too much nitre-gas in the last chamber; for every thing issuing from it is a total loss. Therefore the last chamber but one is kept strongly yellow or red, in order to advance the acid-forming process, but the last chamber only faintly yellow.

The bottom-acid in the latter, which is usually kept at 50° Tw., or even below, will partly absorb the nitre-gas as nitric acid, and there will not be so much of it lost. This state of the last chamber is attained by giving it much steam; but it will be seen at once that in this chamber very little work can be done unless a very great loss of nitre is suffered; for only if the latter be present in large quantity will the oxidation of sulphurous acid go on all through the chamber. Therefore one of these two things must be done: either a large quantity of nitre must be sacrificed in order to utilize the last chamber, or the last chamber is practically used only for recovering part of the nitre; thus actually a third or a fourth of the chamber-space is sacrificed, and so much less sulphur can be burnt in that set. For all that, the last chamber is not merely a costly but also a very inefficient apparatus for recovering the nitre; even if used as such, very little below 10 per cent., mostly above 10 per cent., of nitre to the sulphur must be employed in order to get a good yield. With poor, badly burning ores, of course, even more nitre is consumed, corresponding to the excess of air.

These considerations will make it evident how much more rational it is to *recover the nitre* by a proper apparatus. By this there is a saving of a fourth, up to a third, in chamber-space, at least one of two-thirds in nitre, and mostly also better yield, because up to the last an excess of nitrous gas is present, and no sulphurous acid can escape oxidation by it. In this way any escape of noxious vapours is also much more completely prevented. The construction of the nitre-recovery apparatus, and every thing pertaining thereto, has been described in the 6th Chapter. Here we shall only describe the way of managing the chambers themselves in this case. Supposing the set to consist of three chambers (the reader will easily reduce this to any other proportion by analogy), the first chamber into which, in any case, both the gas from fresh nitric acid and that from the nitrous vitriol are introduced, whether it be by nitre-ovens, or cascades, or Glover towers, or steam-columns, will always have an excess of nitre-gas. In spite of this the characteristic colour of nitrogen peroxide will not be perceived in the first chamber, both because the sulphur dioxide, likewise present in excess, constantly reduces most of the NO_2 to colourless nitric oxide, and because the formation of sulphuric acid, principally going on in this chamber, generates in large quantities the well-known heavy white clouds. The whole atmosphere of the chamber is filled with these, and, owing to its opacity, its colour cannot be clearly recognized. In the second chamber the atmosphere is already much clearer; and as also there is very much less sulphur dioxide present, a portion of the higher nitrogen oxides will be perceived by their peculiar colour. There is, however, still so much sulphur dioxide present, that the mixture of gases in the second chamber will only show a more or less reddish yellow.

In the third chamber, however (in a set of more chambers, in the last—in a single chamber, in its last portion), the nitre-gas should largely predominate. There should be very little sulphur dioxide here; and before the gas issues out of the chamber into the Gay-Lussac tower the sulphur dioxide ought to be entirely removed from it. This is only possible by a large excess of nitrogen acids; and as, according to previous explanations, there is also oxygen present (5 to 6 per cent. by volume), that excess will consist not only of colourless nitric oxide, but also of red nitrogen peroxide. This is proved by the last chamber showing a dark-red colour, sometimes so deep as to be opaque. Even in the much shallower layer of gas seen in the "sight" of the pipe leading to the absorbing-tower, the red or orange colour ought to be quite decided. Within the chamber the red ought to be not quite transparent, but dimmed by a mist of water.

The *colour of a chamber* can be observed by opening the man-lids on the top or the clay plugs in its side, but in a much more convenient and accurate way by glass windows put in the sides of the chamber itself (as described, p. 510). As soon as the last chamber gets paler, the cause of this must be sought for. It may be that it has got too much or too little steam or too little nitre; but it is always a sign that something is wrong; and by comparing the other symptoms, especially the strength and the nitrosity of the drips and bottom-acids, the special cause of the fault must be got at. When the last chamber becomes quite pale, it is certain that a great loss is suffered by sulphur dioxide escaping from it; and the latter, on its way through the Gay-Lussac tower, will even denitrate the nitrous vitriol contained therein, and cause a loss of nitre in the shape of nitric oxide escaping into the outer air. Every thing must therefore be done to avert the above phenomenon.

Apart from the colour, the gradual diminution of sulphur dioxide and increase of nitrogen acids in the chamber-gas as it proceeds on its way can be perceived from other signs, such as the *smell* and the *chemical analysis* of the gas. The judgment by smell is so much more uncertain and inexact than that by colour that it is not worth while to enter upon it in detail. A chemical analysis of the gas would certainly permit the reaction in the individual chambers to be traced with ease and safety; but this plan is not usual, and even the best Continental works only make two gas-analyses—that of the burner-gas before entering the chambers, and that of the gas finally leaving the apparatus as it issues from the Gay-Lussac tower. It would give some little trouble to analyze the chamber-gas between as well; nor is this necessary, since its colour gives a sufficient indication for the purpose in question.

Along with testing the *chamber-acid* for its strength, it is of great importance to test it also for its *nitrosity* (percentage of nitrogen acids); and this forms a necessary complement to the observation of the colour of the chambers. Under normal circumstances the percentages of nitrous acid (or rather of nitroso-sulphuric acid) and of nitric acid in the chamber-acid are so small that its quantitative estimation by the usual method is very inaccurate, especially because a number of impurities interfere with the accuracy of the process. In practice, however, a simple and momentarily made *colorimetrical test* with ferrous sulphate is sufficient for the object in question.

When a solution of ferrous sulphate is poured upon the drip- or chamber-acid contained in a test-tube so that the liquids are not mixed, a yellow ring is formed at the point of contact, if traces of the higher nitrogen oxides are present. With more nitrogen oxides the ring becomes darker; with still more the whole ferrous sulphate solution assumes a deep brown or black colour. In this case effervescence readily sets in, the liquid getting hot, and the dissolved nitric oxide, with the black colour, being driven off by the heat. With some practice, and always working exactly in the same way, it is quite possible to get a good idea of the percentage of nitre in the chamber-acid by its appearance under the above conditions. The testing for a set of four chambers can be carried out in this way:—A stand containing eight ordinary test-tubes of 5 inches height is once or, preferably, twice a day taken to the chambers, and the tubes filled up to about 4 inches with samples of the drip- and bottom-acids of each chamber; at the same time the strength of each sample is taken by the hydrometer, and written on the stand at the bottom of each tube. The acid-samples are then tested, at any convenient place, by carefully pouring on to each about half an inch of a concentrated solution of ferrous sulphate, which need not necessarily be free from ferric sulphate. By looking at the colours produced thereby, in their succession from chamber to chamber, by comparing the drips and bottom-acids, looking at the strengths marked below, and taking into account the colour of the chamber-gas observed through the windows, a tolerably good idea of the process going on in the chambers is obtained. This certainly should be completed by an estimation of the sulphur dioxide in the burner-gas and of oxygen in the escape-gas, and also by testing the nitrous vitriol &c., as we shall see in the next Chapter.

Kolb (Bull. Soc. Mulh. 1872, p. 309) gives a few analyses of chamber-acids confirming what has just been said. They refer to an old-fashioned set without Glover-tower and with nitric-acid cascades.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Density......	1·489	1·417	1·445	1·480	1·488	1·478	1·420	1·457
SO_4H_2	59·1	51·6	54·9	58·1	58·6	58·2	51·4	56·0
N_2O_3	0·023	...	0·04	0·023	0·010	0·02	0·170	0·03
N_2O_5	0·000	...	0·02	0·000	0·000	trace	0·040	0·00
SO_2	...	0·008						

a, acid from the first or denitrating tambour, where the sulphur dioxide of the burner-gas meets the acid of the last chamber and the Gay-Lussac tower; *b*, the same when the chambers were short of nitre; *c*, acid from the tambour where the fresh nitric acid ran over the "cascade" (excess of nitre); *d*, the same, short of nitre; *e*, acid of the "large chamber;" *f*, acid of the last chamber, normal process; *g*, the same, large excess of nitric acid—liquid green and nitrous; *h*, the same, normal process.

The following rules may be laid down for the reactions which the various samples of acid from the chambers and drips ought to show. Generally speaking, all drips ought to show more nitre than the corresponding chamber-acids. The former represent the process going on in the atmosphere of the chamber, whilst the latter should act upon the nitre by their greater dilution, and actually do so. The *bottom-acid* of the *first or leading chamber* ought not to show any nitre whatever; if it does so, it is a strong indication that the supply may be shortened. (It must be borne in mind that a slight quantity of nitre, which can be discovered by finer tests, is nearly always present even in the first-chamber acid, but the above-described rough test ought to show none at all or very little.) But first it must be ascertained if, on the other hand, the drip of this chamber does not show any nitre; for in this case it is proved that there is *too little steam* in the chamber, and that consequently the nitrous acid has been absorbed by the chamber-acid. Mostly this will be confirmed by both drip- and bottom-acid being too strong; and then *more steam* must be given. If, however, *both* samples from the first chamber show nitre, some of the latter must be cut off, unless the supply has just been increased because the last chambers did not show enough; in this case the supply of nitre cannot be cut down till the last chambers have quite recovered.

Sometimes the first chamber-acid smells, on the contrary, of sulphur dioxide; if this is the case to any appreciable extent, nitre is wanting.

The *middle* chambers ought to show already a faint reaction of nitre in the bottom-acid and a stronger one in the drips; the *last*, in any case, a moderately strong reaction in the bottom-acid and a very strong one in the drips. In this case also a deviation from the rule may proceed from various causes. For instance, the last chamber may be pale, and yet its bottom-acid may give a strong nitre-reaction. This may happen both if there is too much and if there is too little steam in this chamber: if the bottom-acid is too strong owing to the want of steam, it will dissolve too much nitre; if, however, there is too much steam present, that phenomenon will take place which, in chambers working without an absorbing-tower, is purposely caused: nitric acid will be formed and will dissolve in the bottom-acid. Both faults are easily avoided if the last chamber is not kept weaker than 90° nor stronger than 110° Tw.; but sometimes insufficient draught may cause these faults as well. If, on the contrary, the last chamber still appears red, and even the drips still show nitre, but the bottom-acid none, this is an indication which must be instantly met by increasing the supply of nitre; otherwise the chamber itself will soon become pale. If both indications coincide, a pale chamber and a ceasing or weakening of the nitre in the drip, this might still be due to an excess of steam; but rarely will it be so, as anyhow that chamber does not get much steam. Three other explanations offer themselves—too little draught, too much draught, or too little nitre. Whether the draught is insufficient is most easily tested by estimating the oxygen in the escape-gas; whether it is too large, by estimating the sulphur dioxide in the burner-gas; but in the case of very leaky chambers, which properly ought to have been stopped already, air enters directly into them, as is proved by the oxygen coming out too high in the escape-gas. Where no gas-analyses are made, the formerly mentioned external indications for judging of the draught are taken into account; but these are far more deceptive than gas-analyses. When the draught is not large enough, the nitric oxide does not meet enough oxygen to be oxidized; it is colourless, and, owing to its insolubility in strong vitriol, is altogether lost. This will be recognized by the appearance of red vapours on the gas issuing out of the chimney, where the nitric oxide is oxidized by the atmospheric oxygen, whilst the chambers themselves, where oxygen is missing, become pale. When there is too much air present, the nitrogen acids are carried away mechanically, and the chambers equally lose ther colour; at the same time sulphur dioxide goes away, as it has not time to be oxidized.

Insufficient formation of sulphuric acid in the chambers, from other causes, such as want of nitre or entering of air through chinks in the chambers and mechanical carrying-away of gas, will frequently *react upon the burners*, since by the insufficient condensation of gas the draught from the burners towards the chambers is diminished. Then all the appearances will take place which are caused by very bad draught in the burners, especially incomplete burning and formation of scars, which, again, weakens the draught. In this case as much nitre as possible must be given, in order to force a better formation of sulphuric acid; and, if necessary, even the burner-charges must be diminished.

But if the last chamber becomes pale, the draught being in order, and if its acid shows little nitre, it is due to want of the latter, and more of it must be introduced till the normal state has been restored. This will be confirmed by *testing the nitrous vitriol*, which will no doubt show a diminution of its nitre. Undoubtedly several circumstances often act at the same time, and make the process a complicated one. If, for instance, there is too little draught, so that, instead of N_2O_3, only NO or even SO_2 get into the absorbing-tower, not only will the draught have to be increased, but more nitre will have to be given as well, in order to make up for the loss. Just in the same way, when the nitre-gas has been mechanically carried away by an excess of draught (in which case, owing to its dilution, the Gay-Lussac tower cannot entirely retain it), not only will the draught have to be moderated, but more nitre will have to be introduced till every thing is in order again.

An *excess of nitre* is detected by the colour of the chambers being too dark, by the strong nitrosity of the acids, and by the fact of the Gay-Lussac acid showing the presence of nitric acid, consequent upon an excess of N_2O_4 in the last chamber.

We thus see that, in nearly every case, when any thing goes wrong in the acid-chambers, an increased supply of nitre is at least temporarily necessary in order to restore the equilibrium, although the other two regulators, steam and draught, must always be taken into account at the same time; it is therefore very important that the possibility be afforded of temporarily introducing much more nitre into the chambers than is necessary in ordinary work; and every factory ought to possess facilities for it. If this should not be the case to a sufficient extent, and if without danger to the chambers it is not possible to introduce as much nitre as the case calls for, then nothing remains but to diminish the burning of brimstone or pyrites for a time, and to allow the chambers to recover their normal state by easing them in this way.

A proposal made by the Manufacture de Javel (E. P. 1752, of 1882) seems to be worthy of more notice than it has received. The nitre is not to be introduced into the leading chamber only, where the temperature may thereby become excessively high, but to a small extent also into the following chambers, whose temperature is sometimes too low. Even the acid for feeding the Gay-Lussac tower is to contain a little nitre, in which case no SO_2 can escape through the tower.

A similar proposal is that of the United States Chemical Company, Camden, N.Y. (Am. P. 325,262, of 1885), to inject nitrous vapours into the last chamber eventually, after having first injected steam, in order to counteract any too strong reduction of the nitrogen-oxides.

Starting from a contrary view, Benker (E. P. 1168, 1895; comp. Kienlen, Monit. scient. 1895, p. 321) injects SO_2 (in the shape of gases from the front of the first chamber) into the last chamber, in order to remedy the drawback, occurring in the "forced work" (*suprà*, pp. 468, 561, 624), that vapours of N_2O_4 are formed which, as he believes, are not sufficiently absorbed in the Gay-Lussac tower. These are to be reduced to N_2O_3 by SO_2. This is evidently the same principle as that involved in Benker and Lasne's former process (p. 626); the only difference is that they injected the SO_2 immediately in front of the Gay-Lussac tower, and that Benker now sends it into the last chamber. In regular work this process might act injuriously; but in cases where there is an excess of N_2O_4 it may do good. According to a communication from the inventor (1902), this process is not applicable where there is a great distance between the first and the last chamber, in which case the SO_2, contained in the gases aspirated from the first chamber by means of the injector, is changed into H_2SO_4 in the connecting-tube.

At some of the best-conducted works it is not thought sufficient to judge of the supply of nitre by the colour of the chambers, the testing of the drips, and so forth, but a system is introduced of constantly checking the amount of nitrous vitriol supplied to the Glover towers, its strength, and the amount of fresh nitre or nitric acid introduced in comparison with the amount of sulphur burnt, in order to keep the quantity of nitre present in the chambers at as constant a figure as possible. As an example of the way in which this account can be kept, I give the following figures, taken from an actual day's work in a well-conducted Continental factory:—

	Set No. I.	Set No. II.
Pyrites charged, kil.	10812	10000
Containing sulphur, less quantity left in cinders	4993	4735
Nitrous vitriol used, kil.	10138	10268
Average strength, expressed in nitric acid 36° B.	4·86	4·37

	Set No. I.	Set No. II.
Equivalent to acid of 36° B., kil.	493	449
Fresh nitric acid supplied, kil.	200	186
Total as nitric acid 36° B., kil.	693	635
Equivalent to 96% nitrate of soda, kil.	520	476
96% nitrate introduced for each 100 parts of sulphur burnt	10·4	10·1

This quantity, about 10 parts of 96% nitrate to 100 of sulphur, may be considered a minimum, and only admissible where the chamber-space is very ample—say, about 24 cub. ft. per lb. of sulphur. With less chamber-space, much more nitre, equivalent to 15 or even 20 parts of 96% nitrate of soda to 100 sulphur burnt per diem, is put through the system. For the high-pressure style in France up to 25 parts of nitre is used; but this involves a correspondingly large nitre-recovery apparatus, without which the waste of nitre would be very serious.

Pemberton (J. Soc. Chem. Ind. 1883, p. 414) quotes a total supply of 15·6 parts of nitre passing through the chambers for every 100 parts of sulphur burnt in the shape of brimstone, with 19·2 cubic feet per lb. of sulphur. In this case a Gay-Lussac tower was used; whilst in three other cases, where there was no Gay-Lussac, from 8 to 10 parts of nitre was consumed, but with 26·8 to 35·7 cubic feet of chamber-space. As he gives no details as to yields, his figures possess very little value.

Benker (commun. 1902) employs as a rule 13 parts total $NaNO_3$ to 100 sulphur burnt in 24 hours. With very well-constructed chambers (comp. his views, p. 459) this quantity may be lowered to 9 or 10 parts, but with wider chambers it must be raised to 18 parts $NaNO_3$. This allows with "high-pressure work" to make 8 or 9 kil. acid of 116° Tw. per cub. metre of chamber-space (say, 0·3 to 0·37 lb. H_2SO_4 per cub. foot). When starting a new set of chambers, the first care is to see that the above quantity of nitre is provided. (Comp. also the statements of Davis, p. 469.)

Irregular Working. Loss of Nitre.

Having so far stated the conditions of the *normal* vitriol-chamber process, we must also consider how the process may become *anomalous*, that is *faulty*, which must, in every case, lead to losses, both of nitre and of sulphur compounds.

Sometimes "free" *nitrogen peroxide*[*] appears in the last chamber (never before). It has been proved by Lunge and Naef (Chem. Ind. 1884, p. 8) that this happens when the supply of nitre is abnormally strong, irrespective of a larger or smaller excess of oxygen, of which there is always far more than enough present. In this case the formation of sulphuric acid is finished before the proper time; there is next to no SO_2 in the last chamber, and the nitrous anhydride, which cannot be again taken up by the chamber-gases, is altogether dissociated into NO and NO_2, the former being equally oxidized to NO_2. The latter where it touches the chamber-acid dissolves in it and forms both nitrous vitriol and nitric acid. Most of the NO_2, however, passes into the Gay-Lussac tower; and as the size of this apparatus is only calculated to meet normal requirements, it cannot retain all the nitrous vapours, but emits a good deal of it into the air in the shape of ruddy vapours, thus causing a corresponding loss of nitre.

Far more serious are the consequences of a *lack of nitre* (comp. pp. 701 *et seq.*). In this case the formation of sulphuric acid is too slow, and there is too much SO_2 in the back part of the chambers, thus causing a denitration of SO_5NH in the *wrong* place. Very much NO is formed, the chambers turn pale yellow, or, in extreme cases, grey, and the temperature is either too high or too low for proper working. Owing to the relative excess of water the formation of the intermediate compound SO_5NH is greatly impaired; and the NO now forms with oxygen and water nitric acid, which sinks down to the bottom and dissolves unchanged in the chamber-acid, and is thus withdrawn from the chamber-process. Such acid will not "show nitre" in the sense used by practical men—that is, it will not give out orange vapours on addition of water, because it contains little SO_5NH, but for all that it may contain so much nitric acid that the chamber-lead is seriously attacked. The nitric oxide, on passing into the Gay-Lussac tower, is not absorbed at all by the sulphuric acid, the excess of inert nitrogen preventing its action with SO_2 and O, and at the top both NO and SO_2 escape, thus causing a double loss. A third source of loss is the formation of nitrous oxide, N_2O, for which the conditions now exist to a much greater extent than normally (see below). All this leads to a bad yield of sulphuric acid from the first and to a great loss of nitre, and as this instantly reacts upon the chamber-process, the floating quantity of oxygen-carriers being diminished at a progressive rate, it is no matter of surprise that things get from bad to worse. Every practical man knows, and Eschellmann has proved it in detail (J. Soc. Chem. Ind. 1884, p. 136), that when there has been lack of nitre from any cause whatever it is necessary to introduce *several times* the amount originally wanting or "saved," in order to remedy the "disease" of the chambers, as some people call it.

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[*] Comp. p. 763 as to the meaning of the term "free" nitrogen peroxide.

Another way in which nitre may be lost is by the formation of *nitrous oxide*, N_2O. We have seen in Chapt. III. (p. 218) that this may happen if NO (or N_2O_3) meets an excess of SO_2 *in the presence of water* or of very dilute sulphuric acid. The reduction may then take place according to the equation—

$$SO_2 + 2NO + H_2O = H_2SO_4 + N_2O.$$

It is not impossible that, under specially unfavourable circumstances, the reduction may even proceed as far as the formation of elementary nitrogen or of ammonia, but this evidently happens only quite exceptionally and to an altogether insignificant extent; whilst most chemists assume the formation of N_2O to occur to a small extent, even in normally working-chambers, at the places where locally water and sulphur dioxide are in excess. Actual proof of this, by showing the presence of N_2O in chamber-gases, has never been given; in fact, the analytical methods so far at our command would hardly permit this.

It is notorious that in no case whatever is the recovery of the nitrogen oxides, active in the manufacture of sulphuric acid, complete. Even with the best nitre-recovery and denitrating apparatus, and under the best possible management, the loss is never below 2 parts of $NaNO_3$ to 100 of sulphur burnt, and it is nearly always higher than that, 3 parts of $NaNO_3$ probably indicating the ordinary present average. The sources of this *loss of nitre* are various, and may be distinguished as mechanical and chemical losses. ***Mechanical losses*** are those caused by incomplete absorption of N_2O_3 or N_2O_4 in the Gay-Lussac tower, by the nitrous acid contained in small quantities in nearly every description of sulphuric acid withdrawn from the process for sale or use, and by any accidental leakages from working-doors, chambers, &c. ***Chemical losses*** are those caused by the reduction of the nitrogen oxides below the point where they can be re-oxidized or absorbed in the Gay-Lussac tower. Generally this chemical loss is ascribed to a reduction to the state of nitrous oxide, or even elementary nitrogen, or (by Raschig) to that of ammonia; but the latter, according to Raschig's own statement, is found only in quite exceptional circumstances and need not be taken into account for ordinary purposes. That a reduction to N_2O does take place under certain conditions (excess of SO_2 and undue local excess of water) has been proved by R. Weber and by myself (p. 218); and it is likely that to a certain extent such conditions do obtain in every vitriol-chamber, but less than anywhere else just in the Glover tower, where such loss was at one time believed to take place (p. 639). It is, however, entirely uncertain what proportion the mechanical and chemical losses bear to each other. The most extraordinary discrepancies exist in this respect. Some chemists assert that the mechanical loss, more especially that caused by incomplete action of the Gay-Lussac tower, is by far the most potent source of loss of nitre (Lunge and Naef, Chem. Ind. 1884, p. 11; Benker; Sorel, Zeitschr. f. angew. Chem. 1889, p. 279; comp. p. 629); others are of the contrary opinion. It seems useless to go into the detail of this controversy here, as no conclusive proof has been given either way, and we will only quote some of the other papers bearing on this question: Hurter, Davis, Jackson, Mactear, Cox, and Lunge, in vol. xxxix. of the 'Chemical News' (pp. 170, 193, 205, 215, 227, 232, 237, 249); Eschellmann (J. Soc. Chem. Ind. 1884, p. 134); Hamburger (*ibid.* 1889, p. 167).

It is a fact that, by enlarging the Gay-Lussac towers beyond the size formerly used, the loss of nitre can be greatly reduced, and mention of this has been made before (p. 580). But it would seem as if the practical limit in that respect had been already reached when the Gay-Lussac towers, with ordinary coke-packing, have a capacity of 2, or at most of 3, per cent. of the chamber-space. Any further addition of absorbing-power causes but an insignificant diminution of the loss of nitre. The cause of this is no doubt that pointed out by Bailey (J. Soc. Chem. Ind. 1887, p. 92), that the coefficient of solubility of N_2O_3 in sulphuric acid is immensely reduced by its enormous dilution in the exit-gases with oxygen and nitrogen, and that therefore a complete absorption of N_2O_3 is an impossibility; Sorel (in the place quoted above) proves a similar reasoning by observation and calculation, showing that, in a special instance, the exit-gases were bound to carry away nitrous acid equivalent to 3·09 per cent. of $NaNO_3$ to 100 of sulphur—that is, more than the best working factories consume altogether, and my observations have accumulated convincing material for such conclusions (p. 227 *et seq.*). It is true that direct analyses of the exit-gases in many instances fail to account for more than a portion (say a third or even a quarter) of the nitre lost; but it cannot be denied that this may simply be an unavoidable fault of the analytical methods used, as it is extremely difficult, or rather impossible, to retain in absorption-tubes all the N_2O_3 or N_2O_4 diluted with ten thousand times its volume or more of other gases. Any reasoning based on the analysis of exit-gases is therefore extremely unsafe, if it intends to prove that the loss from that source is too small to dispense with the necessity of assuming a considerable chemical loss.

It is even more difficult to estimate NO in excess over the proportion $NO + NO_2$ when mixed with a very large excess of other gases, and hence the above-mentioned conclusions are all the more uncertain. The loss of NO may be reckoned partly among the mechanical and partly among the chemical losses. The former is the case when any NO which has come from the chambers themselves has only mechanically escaped oxidation into NO_2 and consequent absorption in the Gay-Lussac tower; but it must be reckoned as chemical loss if the NO has been formed within the Gay-Lussac tower itself by some reducing action on nitrous vitriol. We have seen that such an action may take place by an accidental excess of SO_2 (p. 628); but this happens only exceptionally, although it is possible that the SO_2, always present in exit-gases even with the very best work, in spite of its very slight quantity exerts a certain reducing-action in the Gay-Lussac tower. Hjelt (Dingl. Journ. ccxxvi. p. 174; comp. also our 1st edition, p. 570) ascribed a certain loss of nitre to the oxidation of arsenious to arsenic acid in the Gay-Lussac tower, amounting to 0·12 nitre per 100 of H_2SO_4 made, and Davis (Chem. News, xxxvii. p. 155) went even much further in that respect; but the latter did not uphold his views later on, and even Hjelt's observation seems to have been quite exceptional, to judge from observations communicated to me in a letter from Dr. Th. Ernst, of Lehrte. Evidently arsenious acid can play but a very small part indeed in that matter.

A more important part in the loss of nitre is borne by the *coke-packing* of the Gay-Lussac towers. I had long ago (comp. p. 231) proved that the coke reduces any nitric acid getting into the Gay-Lussac acid in the shape of N_2O_4, so that the nitrous vitriol issuing at the bottom contains only N_2O_3. I have shown (in the same place) that nitrososulphuric acid itself is reduced by coke, NO escaping. This action is greatly increased by a higher temperature, and this may be one of the reasons why it is expedient to cool both the gases and the absorbing-acid as much as possible; it also seems to favour the use of Gay-Lussac towers containing a non-reducing packing (p. 586).

Temperature.

At every sulphuric-acid works the *temperature of the chambers* is a subject of constant observation on the part of the attendants, and it is generally understood that the regular and economical working of the process is intimately connected with keeping the temperature at a certain height, different in different parts of the same set of apparatus, and considerably varying in analogous parts of the apparatus at different works, but to be kept as nearly as possible equal and constant in the same place. The care with which the observations of temperature are made certainly varies very much. In Germany for many years past thermometers have been fixed in several parts of the chambers, generally near the "drips" (p. 508), and their readings are regularly recorded. In France and particularly in England this has been very much less the case; even in large and otherwise very well-managed works chamber-thermometers were frequently not to be found even in recent times, and it was often thought sufficient to test the temperature of the chambers by putting the hand upon the lead. It is hardly necessary to say that the latter plan is decidedly faulty, and the small expense and trouble of applying and using thermometers ought never to be shunned.

This is independent of the question, whether a certain temperature is or is not the theoretically best for the process of sulphuric-acid making, and whether this is the *cause*, or the *effect*, of the economical working of the chambers; for there is no diversity of opinion as to the fact that all causes leading to a faulty process act either directly or indirectly on the temperature of the chambers, and that the observation of the latter is one of the most important guides for judging of the proper working of the acid-making process.

Considerable diversity of opinion exists concerning the best temperature for the chamber-process; but there is no doubt as regards some general facts. The temperature of each chamber diminishes from front to back, and naturally even more that of the last chambers compared with the first. All these differences in the normal process ought to be constant. The first chamber will be generally so hot that one cannot touch it for any length of time, say 50° to 65° C.: in the absence of any cooling-apparatus, Glover tower, &c., the heat becomes so high that the lead cannot be touched with impunity; but in that case the chamber will not last very long. The second chamber mostly shows on the outside hardly more than blood-heat; thermometers with their mercury-vessels inside the chambers show from 40° to 60° C. The third chamber, if it be the last, will outwardly show little or no difference in temperature from the surrounding atmosphere; inside its temperature varies from 40° to 30°, and below that.

At the Aussig works in September the tambour showed 60°, the large chamber in its first part 45°, in its last part 43°; the first back chamber 30°, the last (kept without any steam) 20° C.

At Stolberg (1902) the maximum temperature in the front part of the first chamber was 70° to 80° C. in summer, and 10° or 15° less in winter.

At Oker, in 1891, during the cold season, the first chamber showed 70° in front, 60° in the back; the second chamber, front 50°, back 44°; the third chamber, front 35°, back 25°. During the summer season the temperatures are 10° to 15° higher in the front, 5° to 10° higher in the back part.

At Salindres the leading chamber is kept at an average of 65° in summer, of 55° in winter. This is a refutation to the assertion of Favre (Monit. scient. 1876, p. 272), according to whom in the south of France the chamber-process is already disturbed at 65°. But it is true that many skilled chamber-managers prefer working the leading chamber as nearly as possible at 50° to 60° only.

Dr. Stahl informs me that in a set of three chambers for brimstone, working without a Glover tower, but where part of the heat of the burner-gas was employed for concentrating acid, as shown *suprà*, p. 277, the temperature ranged as follows:—

In the first chamber, near the entrance of the gas, from 80° to 90° C., according to the outside temperature.

In the second (main) chamber in the middle from 50° to 60° C.

In the third chamber about 10° C. above the outside temperature in summer, and 20° C. in winter.

The numerous observations communicated by Crowder (Journ. Soc. Chem. Ind. 1891, p. 301) contain nothing of importance.

The opinion expressed by H. A. Smith, according to whom the best temperature would be nearer 100°, is not based on any valid reasons, and seems to be shared by very few practical men ; on the contrary, such high temperatures are universally assumed to be extremely injurious to the chamber-lead and are carefully avoided. In Europe 90° or 95° is probably the maximum temperature employed anywhere; but in America I found in one place, where zinc-blende was burned, a temperature of 100°, and it was asserted that this chamber (of course, the first of the series) suffered less than the last; but they had only a few years' experience at that works, so that we cannot accept the statement as conclusive.

The *lower* limit of temperature is by Schwarzenberg put at 40° to 50° C., because otherwise there would not be a sufficient quantity of water remaining in the state of vapour; he asserts that in cool weather a set of chambers is less easily started than in warm weather, and that in winter more nitre is used than in summer. I must contradict this assertion of Schwarzenberg's, both from his own and from many other practical men's experience. Unless the temperature of the chambers sinks so low that ice is formed in them (which may happen with back chambers kept without steam), no excess of nitre is required in winter; on the contrary, at all well-managed factories known to me it is asserted that they regularly require less nitre in winter than in summer, and that the work altogether proceeds better in the cooler season.

We have also seen (p. 538) that it is a mistake to assume that the water exists principally in the state of vapour within the chambers.

A most remarkable case is presented at the Freiberg works, where the cooling of the burner-gas, in order to condense the arsenious acid, is carried on so far that the temperature is that of the outer air, and in winter the gases often enter the chambers at 0°. In spite of this, no inconvenience is felt, and no special contrivances or precautions need be employed ; the temperature within the first chamber soon rises to 60° and upwards.

On the other hand, it cannot be doubted that there is at all events an upper limit, beyond which the temperature of the chamber ought not to go. We have seen in Chapter III. (p. 227) that with the same gaseous mixture a comparative slight rise of temperature, from 70° to 80°, is sufficient to convert the oxidation of NO to N_2O_3 into a reduction of N_2O_3 to NO. Unfortunately we do not yet know the conditions of the process to the extent necessary for *à priori* fixing the upper limit of the temperature of the chambers with any approach to certainty.

In normal circumstances the temperature of the first (leading) chamber will have a direct relation to the quantity of work put upon the system. Whilst with the ordinary allowance of 20 cubic feet per lb. of sulphur the normal temperature is, as before stated, from 50° to 60°, or at most 65°, it is, with forced work (15 or 12 cubic feet per lb. of sulphur), 80° at the inlet and rises to 90° or 95° further on ; even at the outlet it is still 15° or 20° over the temperature of the ambient air.

Benker (communication 1902) considers a difference between the inside and outside temperature in the last chamber = 10° C. as a mark of excellent work, 18° or 20° should be never exceeded. He regularly fixes a thermometer on the outside as well as one inside, a course much to be recommended.

The temperature of the chambers depends upon various causes. It is raised by the heat of the burner-gases, by that of the steam introduced, and (in a far greater ratio) by the chemical reactions of the acid-making process; sometimes, in warm countries and in unprotected chambers, by the heat of the sun. Part of this heat is withdrawn by the radiation from the thin and quickly conducting leaden walls of the chamber, also by the heat contained in the escaping gas and in the acid drawn off. The loss of heat by radiation will vary according to the season, to the wind, &c., but, of course, much less with chambers enclosed in buildings than with those exposed to the weather. As for a given time both this influence and the heat brought in by the burner-gases and withdrawn by the exit-gases and the acid manufactured vary but little, the inner temperature will practically be governed by the intensity of the chemical reactions.

The facts now stated prove by themselves that, as I have urged before, *frequent observations of the temperature of the chambers are of great importance for the proper management of the process.* Although the temperatures at the various parts of the apparatus show very great discrepancies at different works, they are almost constant in the same set of chambers, so long as everything is in good working order; and for this reason any considerable rise or fall of the thermometer, to the extent of say 5° C., is a certain sign that there is some irregularity which should be remedied. This indication is all the more valuable as it is instantly observed without requiring any tests or loss of time, and it is accessible to any ordinary working-man without the aid of a chemist.

One of the most systematic observations of the temperatures in different places of a set of chambers was made at the Uetikon works by Lunge and Naef (Chem. Ind. 1884, p. 17). Three readings were made every day, and the following are the averages of a prolonged period, both for (A) Moderate duty of chambers (4·4 tons pyrites for 129,000 cubic feet, or 29 cubic feet per lb. of sulphur), and for (B) Intense duty of chambers (6 tons pyrites, or 20·8 cubic feet per lb. of sulphur). The strength of the acid in the "drips" fixed near the thermometers is also indicated. The extreme variations of the chamber-temperatures, of which only the averages are given here, did not exceed 3° or 4° C. The temperature of the outer air varied far more, viz., 3° to 17° in the 14 days' working of A, and from 5° to 20° C. in the 10 days' working of B; but this did not influence anything except the last chamber. The chambers had all the same width (28 feet 4 in.) and height (23 ft.); but the leading chamber was 138 feet, the second 65½ feet, and the third 36 feet long.

	A. Moderate duty.		B. Intense duty.	
	Temp. °C.	Strength °Tw.	Temp. °C.	Strength °Tw.
Pipe coming from Glover tower	65	—	75	—
Front of leading chamber, near bottom	60	123	69	123
Middle „ „ near bottom	60	112¼	71	116
„ „ „ midway up	61·8	—	73	—
„ „ „ near top	64·5	116	76	116
Pipe between first and second chamber	45	119½	57	—
Second chamber near bottom	32	116	41	116
Pipe between second and third chamber	27	—	35	119½
Third chamber	19	116	24	116
Outer air	9	—	12	—

This shows in the first chambers a difference of from 9° to 12° between moderate and intense duty of the chambers. The temperature was very distinctly influenced by the quantity of nitre: with strongly red chambers it was much higher in the front than in the back part; with paler chambers the difference was less, the reaction also going on more equally. At the top of the first chambers the gases were from 4° to 5° hotter than at the bottom, but gas-analysis showed that the gases were not richer in SO_2 and O in the former than in the latter case.

Further experiments were made on the cooling-influence of the radiation from the chamber-walls. The following are the averages of seven days' observation at distances of 10, 4, and 2 inches from the chamber-side, with an average outer temperature of 19°:—

	Distance from chamber-side.		
	10 in.	4 in.	2 in.
	°	°	°
Pipe from Glover tower	78	—	—
Front of leading chamber	72	71	69
Middle „ „ near bottom	74	73	70
„ „ „ midway up	76	75	73
„ „ „ near top	80	79	77
Second chamber	52	51	50
Third chamber	33	33	33

At an outer temperature of 19°, therefore, the cooling between 2 and 4 inches from the chamber-side averaged only 2°, between 4 and 10 inches only 1°. At lower outside temperatures of course the cooling action would be somewhat stronger. Greater differences were found when the following observations were made in the centre of the chamber by lowering a maximum thermometer by means of a wire through the chamber-top and reading off at the other places as before (the table gives the average of ten observations, at an average outside temperature of 18°):—

Pipe from the Glover tower	73°
Front of leading chamber	69
Middle of ditto, 10 inches from side, bottom	70
„ „ „ „ midway up	72
„ „ „ „ top	76
„ „ centre of chamber, bottom	75
„ „ „ „ midway up	78
„ „ „ „ top	80
Second chamber	50
Third chamber	29

This shows a difference of 5° between the centre and a place 10 inches from the sides, so that there would be 8° between the centre and the sides. This would seem to indicate that the hot current moves less quickly in the centre than near the sides, and it agrees with the fact that the percentage of SO_2 and O in the centre is greater, that is, that the reaction is less advanced there than near the sides in the same transverse section of the chamber. This would agree both with the theory of Abraham (to be mentioned further on), according to which the gases move in a spiral course from the front to the back end of the chamber, and with that of Sorel, as we shall see in Chapter IX.

The preceding observations clearly show that the chemical reactions produce a rise of the temperatures, as the heat of the gases in the middle of the leading chamber near the top exceeds even that of the gases arriving in the Glover tower, in spite of the cooling action of the air traversing a distance of 70 feet from the front to the place of observation. This is confirmed by special observations in the fore part of the chamber, where the formation of acid is most energetic:—

	Bottom.	Midway.	Top.
33 feet from front end ...	80·5°	83°	81°
66 „ „ „ ...	75	78	80

Special interest is also afforded by observations made to ascertain the effect of using either *steam* or a *spray of liquid water* for feeding the chambers.

	Steam. (Outer temp. 12°.) °C.	Water-spray. (Outer temp. 24°.) °C.
Pipe from Glover tower............	69	73
Leading chamber, bottom.........	71	73
„ „ midway.........	73	75
„ „ top	76	78
Pipe from first to second chamber	57	68
Second chamber..	41	53
Pipe from second to third chamber	36	47
Third chamber	24	31

It is true that in the second case (water-spray) the outer temperature was 12° higher than when using steam; but we have seen above that this influences especially the first chambers but little, and we may thence conclude that there is no sensible difference in temperature between the application of water as steam or that as liquid spray. All this confirms the paramount influence of the chemical reactions.

Fig. 304.

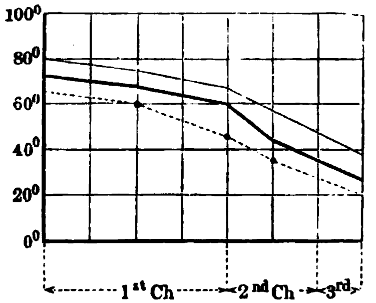


Fig. 305.

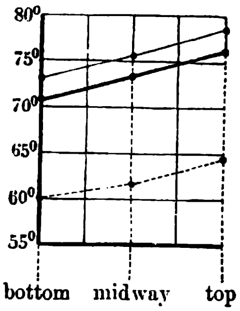


Fig. 306.

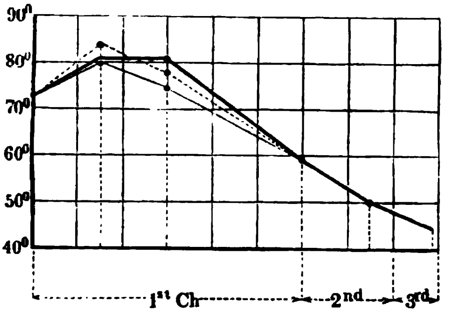


Fig. 307.

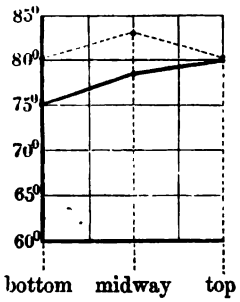
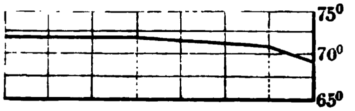


Fig. 308.



The above diagrams, figs. 304 to 308, show the just-mentioned results graphically, the length of the chambers being approximately represented. In fig. 304 the thick line represents the temperature-curve for a normal duty (20·8 cubic feet chamber-space), at 12° C. outer temperature; the dotted line for moderate duty (29 cubic feet), at 9° C. outside; the upper faint line the temperatures observed with a liquid water-spray at 24° outside. Fig. 305 gives the temperatures, obtained in the same series of experiments, as observed in the same transverse section near the bottom, midway, and near the top (the lines have the same meaning as in the preceding figure). Fig. 306 shows the temperature-curves in the longitudinal section of the chambers; the dotted line representing the observations taken at midway height, thin line the bottom, and the thick line the top. They show very clearly how the temperature is raised by the chemical reactions; near the bottom and at a midway height it begins to fall in the second quarter of the leading chamber, but at the top it keeps up as far as midway. Fig. 307 shows the temperature at different heights in the centre of the first chamber; the dotted line at a distance of 33 feet, the thick line at 66 feet from the front end. Fig. 308 shows the increase of temperature from the outside towards the inside (cooling action of the walls).

Eschellmann (J. Soc. Chem. Ind. 1884, p. 135) has proved numerically the relative importance of steam and nitre in the temperature of the chambers.

Taking the drips in the first chamber = 130° Tw., this corresponds to the compound H_2SO_4, $2\,H_2O$ (molecule = 134), or to an evolution of 53,480 + 9,418 = 62,898 calories for 134 grams of that acid. The 54 grams of steam, at 125° C., required for forming H_2SO_4, $2\,H_2O$, represent 34,809 calories. We will now assume that more steam is introduced, and we will put an extreme case, viz., the formation of H_2SO_4, $3\,H_2O$. This means another 18 grams steam at 125° = 11,603; whilst by the reaction H_2SO_4, $2\,H_2O + H_2O$, 1,729 calories are evolved. We must, however, deduct the heat corresponding to a chamber-temperature of 50° = 50·087 calories per gram of water, which is left in the product, and we thus arrive at the following figures:—

The formation of:

H_2SO_4, $2\,H_2O$ evolves 62,898 + 32,105 = 95,003 cal.
H_2SO_4, $3\,H_2O$ „ 95,003 + 10,702 + 1,729 = 107,434 cal.

Taking the gas entering the chambers to contain 6 vols. SO_2 in 100, this means introducing in the first case 3 × 6 vols. H_2O, and increasing the total to 118 vols.; in the second case 4 × 6 vols. of water, or a total of 124 vols. Thus we have—

For 118 vols. an evolution of 95,003 cals.; 1 vol. = 805.
„ 124 „ „ 107,434 „ ; 1 „ = 867.

Now taking the chamber-temperature at 50°, the outer air at 15°, the difference of 35° must be produced by the above reactions. The proportion 805 : 867 : : 35 : 37·6 shows us that introducing so much more steam that the quantity of water in the sulphuric acid is increased by a whole molecule (and thus bringing down the drips from 130° to 110° Twaddell) makes a difference of only 2°·6 C. in the chamber-temperature. The maximum variation produced by changes of the outside temperature, even in summer, when they are greatest, were not found to exceed 5° C. On the other hand, the following observations were made concerning the influence of the *nitre* on the chamber-temperature. Two sets of chambers, burning about equal quantities of pyrites, were supplied with their nitre exclusively by means of nitrous acid from Gay-Lussac towers, and therefore in a continuous fashion, while all the potting of fresh nitre was done in a third, larger, set of chambers, at intervals of two hours. Now the two small sets show no variation of temperature except what is due to the variation of the surrounding air, namely, between 50° and 53° C.; but the large set shows a regular variation from 48° to 68° C., the lowest temperature occurring immediately before potting, when the first chamber is least supplied with nitre, and slowly rising after the potting of fresh nitre. The thermometers were inserted at a distance of 22 feet from the gas-inlets; the temperature of the gas entering was 35° C. The difference between the small, continuously supplied sets, and the large, intermittently supplied set, so far as temperature is concerned, cannot be ascribed to any other cause than the continuous or intermittent supply of nitre. This was conclusively proved by a special experiment in which one potting was missed, so that the only supply of nitre to that set came from a small quantity of nitrous vitriol running down the Glover tower, amounting to but 20 per cent. of the regular supply. In this case the temperature of the gases, entering at 35°, rose only to 41°, the strength of acid at the drips fell rapidly, a large escape of sulphur-dioxide took place at the Gay-Lussac tower, and the chambers worked very irregularly, until not only the missed nitre was put in, but an additional quantity required to compensate for the nitre lost by reduction to nitrous oxide. Eschellmann's experiments are a strong argument in favour of the Continental plan of feeding the chambers with nitric acid.

Sorel (Zeitschr. f. angew. Chem. 1889, p. 271) finds that the difference of temperature between the front and back end of the first chamber, measured 5 feet above the bottom, is only 2°, which is accounted for by the fact that the heat produced by the chemical reactions is only slowly abstracted from the gases by radiation from the walls. The space close to the lead walls is, of course, coolest (comp. p. 718); from here towards the interior of the chamber the temperature increases quickly, and in many cases reaches a maximum at a distance of from 4 to 6 inches from the wall; after this it first sinks and then generally rises again towards the centre. Unfortunately, not many observations were made; but we will quote that series which is fullest (the temperatures, as remarked by Sorel himself, were extremely high, the season being very hot):—

Close to the lead	78°·5 to 79°·7
At 2 centimetres distance	84
„ 4 „ „	91
„ 6 „ „	95·25
„ 8 „ „	95·25
„ 10 „ „	98·3
„ 12 „ „	97·3

Sorel believes that this difference of temperature is strong evidence in favour of Abraham's theory of the path taken by the gases within the chamber (see below); he also makes a most important use of it in his own theory of the formation of sulphuric acid (comp. below).

We must also mention an abnormal state of things which is sometimes observed, namely, a rapid sinking of the temperature of the first chamber, whilst that of the last chamber rises far above the proper degree. This is always accompanied by the colour of the gases getting paler, first in front, then also behind, so that even the last chamber may become quite grey. At the same time there is a great deal of liquid condensing on the glass of the "sights." Ultimately the quantity of sulphur dioxide going away unoxidized may become so large that the nitrous vitriol within the Gay-Lussac tower is denitrated, and the nitric oxide escaping, on contact with the air outside, forms dense red clouds. This state of things is brought about by all the causes which disturb the proper process—want of water, want or excess of steam or of air: all of these tend to keep the process back, so that the first chamber does too little, and the last chamber too much work. An examination of the composition of the gases at the inlet and at the outlet, as well as of the strength and nitrosity of the drips, will lead to localizing the cause of the disaster and admit of applying the proper remedy. Usually, together with all other remedies, a fresh supply of nitre must be given, in order to get up the temperature of the first, and reduce that of the last chamber; that is, to bring back the maximum of production to its proper place in front of the apparatus. Where it is impossible to get enough fresh nitre into the chambers, the pyrites-burners must be kept back, to diminish the amount of sulphide dioxide in the chamber atmosphere. At all events, the indications of the thermometer in the *last* chamber are very important; if it rises above the normal point, the proportion of sulphur dioxide to that of the nitrous gases and steam is sure to be wrong, and should be remedied at once before more mischief is done.

Depth of Acid.

It is a general belief among practical men that the *depth of acid at the bottom of the chamber* influences the completeness and regularity of the chamber-process. In their opinion the best yield and the most regular work is only obtained by keeping a good stock of acid in the chambers, say nine inches or more. On the contrary, a very experienced acid-maker, M. Delplace, emphatically denies that the process is improved by a great depth of acid. He was in a position to start a chamber (whose sides were burnt to the bottom) without any acid at all: the drops could be heard to splash upon the lead as they fell down; yet both the yield of acid and the consumption of nitre (1 part to 100 rectified O.V.) were as favourable as in any other case. It must not be overlooked that a very great depth of acid diminishes the available chamber-space.

I for my part am inclined to favour the view that it is of great importance for the regularity of the chamber work to keep a somewhat deep layer of acid at the bottom of the chambers. The probable cause of this is the fact that this layer serves as regulator for the variations of strength and the percentage of nitre in the acid directly connected therewith. This view is completely confirmed by observations communicated to the 30th Alkali Report, p. 66, by Mr. R. Forbes Carpenter. At a factory where the chamber receives its nitre mostly in the shape of waste acid from the manufacture of nitro-toluol, a film of nitro-toluol is formed on the surface of the chamber-acid, and this shutting-off of the acid from the atmosphere of the chamber causes exactly the same irregularity in the working of the chamber as a low depth of the acid would do. The latter no doubt mainly serves as regulator for the nitre.

My opinion in this respect is altogether shared at Stolberg (1902).

General Remarks.

In checking the process it must never be overlooked that the same symptom may be owing to various causes. Thus the acid may get weaker either by a falling-off in the make or by too much steam. The draught may be lowered either by a smaller make, or by atmospheric influences, or by the gas-flues getting stopped up with deposit. An insufficient conversion of sulphur dioxide into sulphuric acid may be caused by too weak or too strong a draught. The nitre may decrease in the chamber both from an excess of steam, which leads to formation of nitric acid, and from a deficiency of it, leading to chamber-crystals getting dissolved in the bottom-acid; and in both cases the strength of the vitriol falls off. From the fact that in acid-making a certain effect may be caused by different circumstances, the management of chambers is not an easy task, but requires great judgment and experience.

Distribution of Gases and Rate of Formation in the various parts of the Vitriol-Chambers.

The following observations and considerations possess far more than a merely theoretical interest. They are intimately connected with the questions—which is the best shape for vitriol-chambers? are contact-surfaces for the better condensation of the acid to be provided, in addition to mere chamber-space? what is the real duty performed by the various parts of a set of vitriol-chambers, and can that duty be performed in a more advantageous way? and so forth. These questions have been treated at considerable length in preceding chapters (especially pp. 472 *et seq.*), and they will also influence the theory of the Sulphuric Acid Manufacture (comp. below).

The experiments made by H. A. Smith, and recorded in his pamphlet, 'On the Chemistry of the Sulphuric Acid Manufacture' (London, 1873; comp. *suprà*, p. 454), are entirely untrustworthy, as pointed out several times before, in more detail, in the first edition of this work, p. 285 *et seq.* His conclusion, that the chief portion of the acid made in the chambers is produced and condensed close to the surface of the acid already formed in the chambers, has not been confirmed by any other observer, and we will not detain ourselves any further with it, as it is also in direct contradiction to his own analyses of the gases. Hasenclever (A. W. Hofmann's Report on the Vienna Exhibition, vol. i. p. 178) fixed lead dishes in several parts of his chambers, covering them over at a distance of a foot, and thus found that about the same quantity of acid was formed all over the chamber. [This conclusion certainly cannot be proved definitely in this way, as the dishes act as contact-surfaces ; see pp. 473 & 724.]

Mactear (J. Soc. Chem. Ind. 1884, p. 224) has published an extensive series of observations on the distribution and condensation of the gases in the vitriol-chambers. So far as they go towards settling the point at which part of the chamber the principal formation of the acid takes place, they are of no use to us, as they were based on a wrong principle, viz. that of observing the quantity of acid condensed on trays of a certain surface. It has been frequently shown, and that by Mactear himself in the same paper, that solid (or liquid) surfaces within the chambers have an intense condensing action upon the acid, which means that the mist of impalpably small drops on striking such surfaces condenses into large drops and collects upon the trays ; hence the quantity of acid running away from the trays is not that made in the space above them, but represents a very much larger quantity, made partly, and possibly to the greatest extent, at some distance from the place where the tray is located.

How unreliable is the plan of testing the amount of sulphuric acid formed in a special part of the chamber by means of collecting-trays has been very clearly shown by Naef (Chem. Ind. 1885, p. 287). The condition supposed to exist by previous observers is this, that the trays collect all the acid formed in the vertical space above them. If it were so, next to no acid would be found when the tray is provided with a cover. If, however, the drops fall down in a slanting direction, some acid will be found, and its quantity ought to vary in proportion to the distance between the tray and the cover. But even this is not the case. Naef placed within the chamber on one side an open tray, and on the other side a tray with a wider cover suspended over it at a variable distance. The result of weekly averages was this :—that the tray with the cover 12 inches above it collected exactly as much as the open one, and even when the cover was only 4 inches above the tray the acid collected was nearly as much as on the open tray. Repeated observations confirmed this result entirely. This surprising phenomenon cannot be explained by a slanting fall of the drops, for it would suppose the fall to take place at an angle of 20°, which cannot be produced even by the most violent movement within the chamber, far above anything which really exists. There is no other explanation than one to which a very large number of former observations in all possible cases, also those of Mactear, irresistibly lead—that the sulphuric acid, when formed, exists in the shape of a very fine mist which is very slowly deposited in the form of a rain of real drops, and is carried forward by the gases for long distances, but is suddenly condensed to real drops when striking against solid [or, perhaps, liquid] surfaces. Therefore the acid is not deposited at all in a liquid state where it is formed, but further on, in very different quantities according to the surfaces it meets; hence the apparent contradictions between the results of gas-analyses and those of measuring the acid condensed on trays. The latter mode of observation is utterly worthless for deciding the question of the progress of the chemical reactions ; this progress must undoubtedly be studied by gas-analyses. This last method presupposes that the gases in any special transverse section of the chamber are somewhat, although not absolutely, equally mixed; but that this is so, has been proved by the results of Lunge and Naef (see later on) as well as by those of Mactear himself. The fact that nearly as much liquid acid is condensed on the trays near the top as upon those near the bottom of the chamber is easily explained by Abraham's theory of a spiral movement of the gases (see below), of which it is, indeed, a necessary consequence.

Hence we cannot accept Mactear's conclusion that the principle part of the acid is made in the upper portion of the chamber. In fact this does not agree with his own analyses of the chamber-gases, and even less with his further conclusion (p. 228 of his paper) that the principal condition is that of "having ample chamber-space, the form of the chamber not being so material." The argument that the sulphuric acid forming and falling rapidly towards the bottom of the chambers must displace the gases and force them to the upper portion is fallacious; for the volume of the acid forming is several hundred times less than that of the gases concerned in its formation, so that the above-mentioned action must be imperceptibly small.

Mactear's observations on the rate at which the acid is formed in different chambers of a set are very interesting. The following table shows the composition of the gases in the different parts of a set of chambers, connected with a Glover and Gay-Lussac tower, calculated from a long series of observations. In the original the figures are given to three decimals per cent., but we reduce them to one decimal, the estimations certainly not being accurate even to that place. The nitre in the original is all calculated as N_2O_4, which is certainly wrong, and looking at the imperfection of former analytical methods, we must accept the figures for nitre with all reserve.

	Gas entering the								Exit-gas.
	Glover tower.	1st ch.	2nd ch.	3rd ch.	4th ch.	5th ch.	6th ch.	Gay-Lussac.	
SO_2	6·3	6·3	4·5	2·6	1·4	0·7	0·3	0·03	0·03
O required to form SO_3	3·2	3·2	2·2	1·3	0·7	0·35	0·11		
N equivalent to Fe_2O_3 and SO_3	45·6	45·2	46·6	48·0	48·9	49·4	49·7	49·9	50·0
O in excess air	9·4	9·4	9·7	10·0	10·2	10·3	10·3	10·4	10·4
N in excess air	35·9	35·8	36·9	38·0	38·7	39·1	39·4	39·5	39·6
N_2O_4	...	0·12	0·12	0·13	0·13	0·13	0·13	0·13	0·01

The next table shows the comparative condensation of acid in the six consecutive chambers :—

No. of chamber.	Acid made.	H_2SO_4 in acid made.	Excess water.	Per cent. of H_2SO_4 made in each chamber.
	Tons.	Tons.	Tons.	
1.	23·52	19·89	3·63	32·20
2.	22·59	18·68	3·91	30·26
3.	20·35	14·89	5·46	24·11
4.	10·23	4·35	5·88	7·04
5.	5·84	3·09	2·75	5·00
6.	2·19	0·86	1·33	1·39

The following table is taken from Mactear's paper, and shows the comparative condensation of the single chambers of various sets of sulphuric-acid chambers:—

Chamber 1.	31·50	32·20	32·5	38·4	34·1	33·8	52·4	63·9	38·7	78·6	53·9	81·8	26·1	32·0
,, 2.	29·27	30·26	24·8	35·2	20·0	42·2	26·4	36·1	33·6	21·4	36·9	17·8	31·3	29·0
,, 3.	18·71	24·11	19·3	15·6	19·7	22·6	16·5	...	12·9	...	9·2	...	20·4	17·5
,, 4.	10·32	7·04	15·5	6·2	18·1	...	...	...	9·8	...	...	...	11·8	13·7
,, 5.	6·45	5·00	5·8	3·2	7·3	...	...	...	3·4	...	...	...	7·9	5·4
,, 6.	3·75	1·39	2·1	1·4	0·5	...	...	...	1·6	...	...	...	2·4	2·2
,, 7.	...	...	...	...	0·3	...	...				...			
Tunnels ...	...	...	...	...	...	1·4	4·7	...	...	...		0·4		
	100·00	100·00	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0

Crowder (J. Soc. Chem. Ind. 1890, p. 302) quotes the results found with gases taken from testing-holes in the connecting-pipes:—

	Lump-ore kilns.		Dust-kilns.	
	SO_2.	O.	SO_2.	O.
From Glover tower to No. 1 chamber.	6·9	8·0	5·2	11·8
,, No. 1 to No. 2	4·4	7·5	2·4	11·8
,, No. 2 to No. 3	1·9	5·7	1·2	10·6
,, No. 3 to No. 4	0·4	6·1	0·6	10·2
,, No. 4 to Gay-Lussac	0·3	5·7	0·4	9·3

Another series from a Scotch works, with a set of 6 chambers:—

	SO_2.	O.
Glover tower to No. 1........	6·32	12·55
No. 1 to No. 2	4·44	11·89
No. 2 to No. 3	2·63	11·28
No. 3 to No. 4	1·40	10·86
No. 4 to No. 5	0·70	10·61
No. 5 to No. 6	0·26	10·46
No. 6 to Gay-Lussac	0·035	10·38

Probably the most extensive and complete investigation on the phenomena taking place in the vitriol-chambers has been made by myself in conjunction with Dr. Naef at the Uetikon Alkali-Works near Zurich, where a set of chambers was placed at our disposal for this purpose during a period of several months. From our Report thereon (Chem. Ind. 1884, p. 5 *et seq.*) I have already quoted in several places, *e. g.* the methods employed for testing the gases (p. 419) and the observations of chamber-temperatures (p. 714). I here give a very short abstract of the important results obtained, which in all essential particulars have been entirely confirmed by a similarly extensive investigation made by Retter at a Hamburg works (Zeitschr. f. angew. Chem. 1891, p. 4 *et seq.*). The set of three chambers observed has been briefly described on p. 714. They were provided in twelve different places with complete sets of absorbing-tubes, large aspirators, and everything else required for making the most detailed and accurate analyses of the chamber-gases hitherto attained *.

The first six experiments proved decisively that in a *normally* working set of chambers, containing a plentiful supply, but no excess, of nitre, the nitrogen oxides in the last two chambers did not contain any "free" nitrogen peroxide †, but their composition corresponded to that of nitrogen trioxide (nitrous anhydride). It had been assumed by Berzelius, and later on by R. Weber and by Hasenclever, that N_2O_3 was the real oxygen carrier, whilst most other chemists assumed that it was nitrogen peroxide; but Berzelius altogether confused N_2O_3 and N_2O_4, and Weber and Hasenclever, although they, of course, clearly distinguished between these two compounds, did not give any proof whatever of their assumption that the nitrous gas within the chambers is N_2O_3, not N_2O_4. The observations and analyses of Naef and myself for the first time gave a basis of fact to the statement that nitrous acid is the real oxygen carrier in the vitriol process. These observations have clearly established the fact that *in a normally working chamber no "free" nitrogen peroxide is found*, and Retter's observations (comp. p. 727) have entirely confirmed this. It is true that it was impossible to distinguish entirely between the single nitrogen oxides in the *first* chamber, as unfortunately no analytical methods are known by which this could be done in the presence of the large quantity of SO_2 existing in that place; all that can be done is to *calculate* the nitrogen oxides either into NO and N_2O_3, or NO and NO_2. But that the former, not the latter, is advisable, is proved by our further experiments, which showed that even when abnormally N_2O_4 was produced in the third chamber, yet the second chamber never contained any "free nitrogen peroxide" *. *A priori* it is also most unlikely that in the first chamber, where the reducing action of SO_2 is so much more potent than in the second and third chambers, the nitrogen should be in a higher state of oxidation than in the latter chambers. It is therefore to be considered a fact *that the nitrogen oxides present in the last chambers correspond essentially to the composition of nitrogen trioxide, accompanied in the first chamber by nitric oxide,* NO.

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* It is true that even these analyses do not represent the absolute facts of the case. Some changes may, and even must, have taken place in the gases on their passage through the absorbing-apparatus; more especially the estimation of NO is not one of the most accurate operations. Nor can it be assumed that the samples of gas aspirated always represented the true average of that part of the chamber; and it was altogether impossible to be sure of following up one and the same batch of gas during its progress through the chambers. Our analyses cannot therefore pretend to be authoritative in all details, but they may certainly be taken as representing the general working of the process. Sorel's criticisms of our methods are not very appropriate, as he does not suggest any better ones; his own plan of analyzing nothing but the drip-acids is altogether misleading, as it takes no notice whatever of the proportions of oxygen and nitric oxide in the surrounding gases; and as it seems, from his description of the process, that he measured the reducing power of the acid by running a solution of potassium permanganate into the vitriol, instead of *vice versâ*, he must have found nitric acid even where none was present, as proved by me in 1877 (Ber. d. deutsch. chem. Ges. vol. x. p. 1074).

† To avoid repetitions, we do not distinguish between NO_2 and N_2O_4, but call the mixture "nitrogen peroxide." "Hyponitric acid" is an antiquated expression. In the following abstract of the observations made in 1883, I retain the expressions "nitrogen trioxide" or "nitrogen anhydride," then considered to correctly denote the facts of the case; but we now know (p. 214) that the N_2O_3 found by analysis is almost entirely dissociated into NO and NO_2 in the gaseous state.

Another set of five experiments was made in this manner, that the quantity of nitre was increased far beyond the normal measure, so that a large volume of yellow vapours escaped from the Gay-Lussac tower. Under these anomalous circumstances, free nitrogen peroxide was found in the third, but never in the second chamber. *The chambers therefore contain free nitrogen peroxide only when the*

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* The expression "free nitrogen peroxide," in this and every subsequent case, means that portion of NO_2 which is in excess over that which is necessary to form N_2O_3 with NO.

*supply of nitre is abnormally high**. The formation of nitrogen peroxide must be regarded as a secondary reaction, brought about in the following way:—With an abnormally high supply of nitre the oxidation of SO_2 into H_2SO_4 is almost entirely finished in the first chambers, as far as it can be driven (which is never up to the entire extinction of SO_2). There is hence very little sulphuric acid floating about as mist in the last chamber, and there is thus no impediment to the oxidation of NO going on to NO_2, which, as we shall see, does not take place in the presence of sulphuric acid. Moreover, the SO_2 still present in the cases here treated is of such minimal quantity (0·0004 to 0·002 per cent.), that its reducing action can scarcely be expected to be felt. The conclusion to be drawn from all this is that *free nitrogen peroxide, being absent in normally working chambers, cannot take any essential part in the formation of sulphuric acid in the vitriol-chambers.*

When speaking throughout this work of "normally" and "abnormally" working chambers, I mean those terms as understood at all English and German works, with a chamber-space of at least 16 cubic feet per lb. of sulphur. In the "forced or high-pressure style" (*production intense*) practised at a few French works, where so much acid is produced in the chambers that only 12 cubic feet of chamber-space are allowed per lb. of sulphur, an excessively large supply of nitre must be given, which at all other works would be called "abnormally high," but certainly is not so under those exceptional circumstances. This leads to the regular appearance of nitrogen peroxide in the last chamber, and perhaps even of nitric acid in the nitrous vitriol of the Gay-Lussac tower. Sorel's statements in this respect are made uncertain by the fault in the analytical method employed by him (comp. above, p. 727, footnote), which would tend to make the proportion of nitric acid larger than it was in reality.

Special experiments made by Lunge and Naef proved the following important facts:—1. Even with an abormally low percentage of oxygen in the exit-gases (4 per cent.) the formation of free NO_2 takes place when an excess of nitre is sent into the chambers. 2. Even with an abnormally high percentage of oxygen in the exit-gas (8·18 to 9·19 per cent.) no free NO_2 is formed when the supply of nitre has been a normal one. This shows that *the*

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* Of course footnote † on p. 728, concerning the expression "free nitrogen peroxide," applies here as well.

quantity of air sent into the chambers has no influence whatever upon the formation of free nitrogen peroxide, which, on the contrary, is *exclusively* caused by an excess of nitre.

In Lunge and Naef's paper there follow experiments on the losses of nitrogen compounds, which will be mentioned later on, and then experiments on the *distribution of the gases and the progress of the process in the chambers.* For this purpose eight sets of absorbing-tubes were fixed in various parts of the chambers, three of which were always worked simultaneously; in each place at least 20 litres of gases were aspirated for every test, the whole being finished within 5 or 6 hours. Five different complete sets of such observations were made, comprising both normal working and shortness of nitre in the chamber.

It would be too lengthy to give all the details of the analyses; they prove the following facts:—When the chambers are working in a *normal* way, the percentage of SO_2 in the gases decreases very quickly, and in the middle of the first chamber has already fallen from 7 to 1·7–1·9 per cent., so that about 70 per cent. of SO_2 must have been converted into sulphuric acid. From here to the end of the first chamber there is very little action, and only 4 per cent. of the original SO_2 is here absorbed. When entering into the second chamber the reaction is suddenly revived, and in its middle the gases contain only 0·2 to 0·4 per cent. of SO_2, 20 per cent. of the initial SO_2 being absorbed here.

Fig. 309.

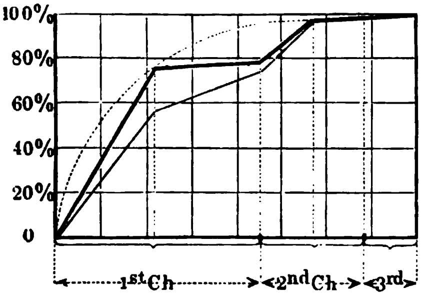
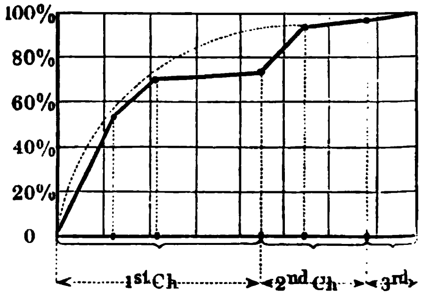


Fig. 310.



From this point to the end of the set the oxidation proceeds very slowly, and never to the point of absolutely extinguishing the SO_2. The diagrams, figs. 309 & 310, show this both for the normal working order (in the thick line) and for working short of nitre (the thin line)—the horizontal lines corresponding to the length of the chambers, the perpendicular lines to the percent. oxidation of SO_2 into H_2SO_4. There is also a dotted curve added, representing the progress of the process according to Hurter's theory (comp. below), which is seen to agree much better with the normal than the anomalous style of working. This agreement comes out still better in fig. 310, representing the results obtained in another, intermediate, testing-place.

These experiments for the first time established a fact, subsequently confirmed by all similar observations, the whole importance of which will appear below, viz., that the *conversion of* SO_2 *into* H_2SO_4 *takes place very quickly as far as the middle of the first chamber, then slackens very much, but is suddenly revived when the gases pass from this into the next chamber.* This fact was at the time explained merely by a better mixture of the gases, but we shall see that this explanation should be supplemented by other, and perhaps even more important considerations; and it has formed the first basis for the practical improvements proposed by myself, as described above (pp. 478 *et seq.*).

The observation made by Lunge and Naef at the Uetikon works, that the reactions after slackening in the last part of the first chamber experience a sudden revival when the gases pass into the next chamber, has been confirmed by later observations of

	1.			2.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*
O	9·63	10·37	8·45	5·15	5·62	5·18
N	89·90	88·89	90·64	92·05	92·26	92·47
SO_2	0·47	0·73	0·91	2·28	1·99	2·18
NO	...	...	...	0·05	0·06	0·06
N_2O_3	...	...	...	0·10	0·09	0·11

	3.			4.			5.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*
O	6·68	6·07	6·04	5·98	—	5·42	6·37	6·27	6·27
N	91·28	91·84	91·90	92·64	—	93·17	91·77	91·70	91·76
SO_2	1·86	1·94	1·88	1·20	—	1·20	1·86	2·03	1·97
NO	0·07	0·06	0·06	0·06	—	0·06			
N_2O_3	0·12	0·09	0·12	0·12	—	0·14			

Naef's at the British Alkali-Works at Widnes (Chem. Ind. 1885, p. 285), by Schertel at the Freiberg Works (*ibid.* 1889, p. 80, and Sächs. Jahrb. f. Berg- und Hüttenwesen, 1890, p. 138), by Sorel (Zeitschr. f. angew. Ch. 1889, p. 270), and Retter (Zeitsch. f. angew. Ch. 1891, p. 4), and this must be looked upon as an established fact, the consequences of which for the theory of the vitriol-chamber process will be mentioned later on.

Another set of experiments referred to the question *how far the gases get mixed up in their progress through the chamber.* For this purpose the gas was aspirated and tested simultaneously from three places, lying in the same vertical line in the side of the first chamber, with the results given in the table on the preceding page (*a*=top; *b*=middle; *c*=bottom).

The differences in composition found between *a*, *b*, and *c* here are certainly but slight.

For the following experiments three lead tubes were passed through the chamber-top in the centre line, on the same cross section as the place on the sides on which the points *a*, *b*, *c* were situated, the three inner tubes reaching down to the same vertical height as the points *a*, *b*, *c*. Gas-tests were taken at all six points at the same time, with the following results:—

	a. Top.		*b.* Middle.		*c.* Bottom.	
	Inside.	Outside.	Inside.	Outside.	Inside.	Outside.
Exp. A.—O	7·34	7·12	7·76	7·36	6·93	7·39
N	90·43	91·07	89·98	90·78	90·71	90·85
SO_2	2·03	1·66	2·08	1·67	2·18	1·58
NO	0·08	0·08	0·08	0·10	0·10	0·10
N_2O_3	0·12	0·08	0·11	0·09	0·07	0·08
Exp. B.—SO_2	2·20	1·96	2·03	1·82	2·04	1·93

The difference in the composition of the gases here also is much slighter than was formerly assumed. More especially it was found that, contrary to former theories, the SO_2 is almost uniformly distributed at top, middle, and bottom. But it must be mentioned that there was, without any exception, considerably less SO_2 found at the outside places, near the chamber-walls, than in the centre of the chamber. This was noticed by Lunge and Naef at the time (*l. c.* p. 17); they distinctly state that it proves that the reaction between

SO_2 and O is rather stronger near the walls than in the centre of the chamber. A full explanation of this fact was only given several years later.

A last set of tests, in three places one above another in the first quarter of the first chamber, showed:—

	Exp. A.			Exp. B.		
	Top.	Middle.	Bottom.	Top.	Middle.	Bottom.
O	6·50	6·26	6·79	5·89	6·07	5·81
N	90·34	90·13	90·14	90·70	90·31	90·86
SO_2	3·07	3·61	3·07	3·71	3.62	3·33

The entering gases had contained 6·6 per cent. SO_2, so that at this place already about 50 per cent. of the SO_2 had vanished only 30 feet from the front end of the chamber.

All these experiments (with which the observations of temperatures, p. 716 *et seq.*, agree) *prove that the gases within the chamber are very quickly mixed up, whatever may be the cause of this, but that the mixture is not an absolutely equal one; there is always more* SO_2 *in the central part of the chamber than on the outside, or at top and bottom.* Retter (comp. p. 727) confirms this.

It must be especially insisted on that the differences between the analyses of various samples of gases are far greater than can be accounted for by analytical errors or by the inaccuracy of the methods; it was distinctly proved that in some parts of the same transverse section there is more SO_2, in some more O, in some more nitre, and it must be inferred without a shadow of doubt that there is in some places more moisture than in other parts of that section. Anybody who has experienced the difficulty of completely mixing two currents of gases even when experimenting on a very small scale will regard this as a matter of course. Those, therefore, who contend that Lunge and Naef's analyses prove an absolutely uniform composition of the gases in the same section of the chamber, and who from this infer the uselessness of a more intimate mixture, are altogether wrong, the above contention being erroneous; Schertel himself (Sächs. Jahrb. 1890, p. 144), who had formerly adhered to the just-mentioned opinion, afterwards found that the mixture of the gases is not at all absolutely perfect.

Thus Lunge and Naef's observations have refuted all the various theories according to which the sulphuric-acid making process either takes place principally close to the bottom-acid (H. A. Smith) or immediately below the top of the chamber (Mactear). They are, however, altogether compatible with Sorel's view (comp. below), which demands a stronger formation of acid near the chamber-walls, and with the views of Abraham (Dingl. Journ. 1882, vol. 245, p. 416), concerning *the path taken by the gases within the chambers*.

After refuting the opinion pronounced by Schwarzenberg, according to which the burner-gases at once rise to the top of the chamber, and then gradually sink down in nearly horizontal layers, Abraham states his own ideas as follows:—The burner-gas, on entering the first chamber, meets a gaseous mixture whose temperature and composition differ but little from its own; it therefore spreads all over the front part of the chamber from top to bottom, and is slowly propelled by the draught along the chamber all over its transverse section. The formation of sulphuric acid also takes place regularly and equally at all points of each transverse section, taken at right angles to the length of the chamber, first rapidly, then more slowly. (This part of Abraham's theory cannot be accepted.) The heat produced by the reaction raises the temperature of the interior, whilst at the side walls and the tops this heat is carried off by radiation outside. Thus is produced a difference in the temperature and the density of the gases which must lead to their rising in the centre of the longitudinal section, and to their descending along the sides of the chamber. Since the cause of this difference of temperature is a constantly acting one, the just described movement goes on through the length of the chamber, and is modified only at the ends, both through their own cooling action, and through the contraction of the current produced by the connecting-pipes. Thus *the gases travel in vertical layers at right angles to the length of the chamber, from the front to the back end, but each single gaseous molecule describes a spiral line, whose axis is parallel to the length of the chamber.*

This is of course only a general expression of the path of the gases within the chambers, and is modified locally by special circumstances; but it accounts for the approximate equality of the composition of the gases and temperatures observed in

Lunge and Naef's and even in Mactear's experiments; Abraham's conception may therefore be accepted as an approximation to the truth.

Carbon dioxide in Chamber-gases.

It is generally assumed by manufacturers that *carbonic acid* exercises a very injurious action in the lead chambers, and it is principally on this account that "coal-brasses" are not considered a good raw material for the production of sulphuric acid (pp. 41, 328). If this is really the case, it is all the easier to understand why the proposals for filling the lead chambers with coke have been unsuccessful. The reason why it should be so is not yet clear. Some practical men assume that the CO_2 forms distinct layers, preventing the intimate contact of the gases with each other and with the bottom-acid; but I am not aware of any direct observations on this point, except in one case where blende containing very much carbonates was worked, when it was found by many gas-analyses that the carbonic acid accumulated in the corners and other "dead" places, whilst the main stream of the gases contained much less CO_2. This subject ought to be further investigated, especially as I know of a Bohemian works where sulphuric acid is made from material containing 10 per cent. of bituminous substances, without any special trouble being experienced.

Duration of passage through the Chambers.

Calculations have been made as to ***how long the gases remain in the lead chambers*** before the manufacture of sulphuric acid is complete. This subject is treated at length in our first edition, vol. i. p. 455 *et seq.*; here we will only mention that Schwarzenberg calculates that the gases pass through the chambers in 5¾ hours, Bode that they take 3¾ hours, and I myself (assuming a chamber-space of 20 cubic feet per lb. of sulphur and burner-gases with 8 per cent. SO_2) reckon 2¾ hours. It is also there calculated that, assuming a consumption of 4 parts of pure sodium nitrate to 100 parts of sulphur burnt, the nitre-gas does its oxygen-carrying work 130 times over before it is lost in some shape or another. Sorel calculates that in a system working on the "high-pressure" plan, with only 0·7 cubic metre per kil., or 11·2 cubic feet per lb. of sulphur burnt (in winter), the gases take only 1 hour 34 minutes to pass through the chambers.

Testing the Chamber-exits.

Apart from the ultimate check on the process afforded by frequent estimations of the yield of acid and the consumption of nitre, of which we shall speak later on, it is very desirable, and is indeed now required by law, to control the quantity of acids escaping from the vitriol-chambers into the atmosphere. So far as "low-level escapes" are concerned, that is the gas blowing out of pyrites-kilns, potting-holes, accidental leaks in the chambers, and so forth, it is not possible to estimate them directly; but it is just these kinds of escapes that are most readily perceived, and although they may be very troublesome to those residing in the immediate neighbourhood, they hardly ever amount to any considerable percentage of the sulphur burned.

It is very different with the gases escaping from the end of the whole system into the atmosphere, whether it be through a simple pipe or a Gay-Lussac tower, or the chimney. These "high-level escapes" may cause a serious manufacturing loss, and they may also amount to a real nuisance for a somewhat wide circle round the works, although in most instances only temporarily, especially in unfavourable weather. Before the introduction of nitre-recovery apparatus the loss, both of the acids of sulphur and those of nitrogen, must have been far more considerable than now, as the whole style of working inevitably tended in that direction (comp. p. 697); but nothing certain can be stated with regard to this, as no observations on the acidity of chamber-exits were formerly made, and at present all well-arranged works do recover their nitre. In this case the losses will not be quite so serious, but they do exist all the same, and that to a greater extent than was formerly supposed.

Among the first who drew attention to the necessity of regularly testing the chamber-exits for their acidity were Mactear (Chem. News, vol. xxxvi. p. 49) and G. E. Davis (*ibid.* vol. xli. p. 188).

Control of the acids escaping from the chambers into the atmosphere has been made compulsory in England, since, in 1881, it was enacted by law that the total quantity of sulphur acids escaping from an alkali-works should not exceed four grains per cubic foot, expressed in terms of sulphuric anhydride, SO_3 (Sec. 8 of the Act). About nitrogen acids or nitric oxide nothing is enacted, probably because the quantity escaping from alkali-works is never so great as to cause a nuisance, but it is all the more important for the manufacturer himself to know how much nitre he is losing in this shape; moreover, in testing the chamber-exits it is but little additional trouble to include the nitrogen acids.

In Germany, by an order in Council of July 1st, 1898, the maximum amount of total acids in the exit-gases of works burning pyrites has been fixed at 5 grams, from blende 8 grams per cubic metre, calculated as SO_3.

The Government Inspector's Reports show that the real escape of acid gases from the exits of sulphuric-acid works is far below the maximum prescribed by the Act. The acids escaping, calculated in grains of SO_3 per cubic foot, were in 1887, 1·500; in 1888, 1·490; in 1889, 1·370; in 1900, 1·198; in 1901, 1·186.

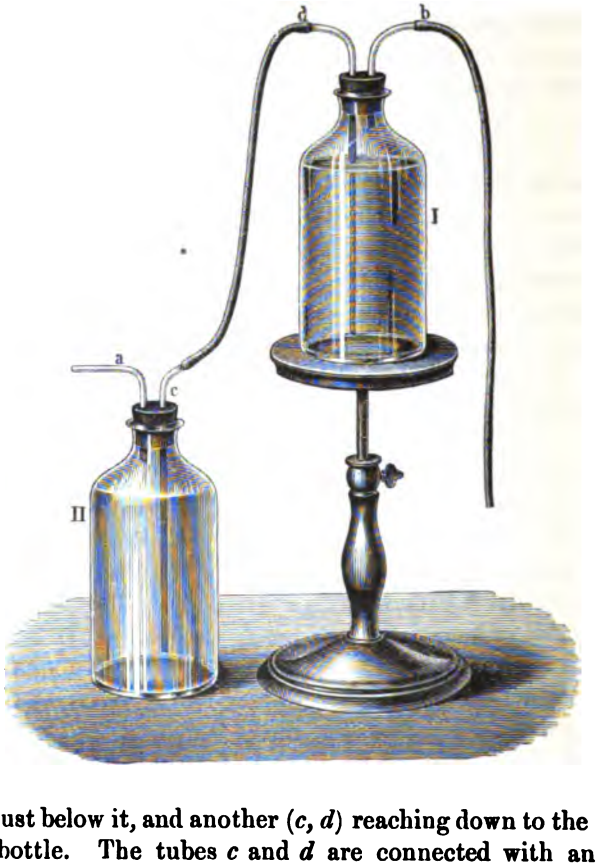
It seems to be lawful, where the gases cannot be sufficiently diluted down to the standard escape by means of fuel gases from other parts of the process, to do this by atmospheric air admitted to the chimney (Alkali Inspector's Report No. 38, p. 76; comp. *suprà*, p. 371).

Two systems may be employed for controlling the acid escapes—that of taking several separate tests through the day, and that of continuously aspirating some of the gas through a set of absorbing-apparatus, and measuring the quantity of gas passed through them.

The unreliability of the first system is too patent to be enlarged upon; it is hardly applicable at all to night-work, to begin with. Hence the continuous-testing system has been generally adopted, and this at many works in the very complete shape given to it by Mr. Mactear (*loc. cit.*). His apparatus consists of a water-jet pump (of the system invented by Dr. Sprengel, but commonly called "Bunsen pump") for aspirating the gases, a set of absorbing-tubes, and a gas-meter to measure the volume of the residual gases after absorption. The whole, including the cocks and connections, is enclosed in a locked closet to prevent their being tampered with. The meter is fixed with an index so arranged that by observing the reading for one minute the rate of passage per hour is given by direct indication, so that the rate of aspiration is easily arranged. Mactear at that time proposed caustic soda and ammonia as absorbents, to be titrated for SO_2 with permanganate; but this would yield quite wrong results, far below the truth, as sodium sulphite is rapidly oxidized by the oxygen passing through the solution.

Mactear's apparatus is very efficient, but it is very costly, and any such delicate apparatus as a gas-meter is very liable to get out of order in such proximity to acid vapours. Hence at most places cheaper and simpler forms of aspirators have been adopted. One of the simplest is represented in fig. 311. It consists of two glass bottles, I. and II., each provided with a twice-perforated india-rubber cork, through which passes one elbow-tube (*a, b*) ending just below it, and another (*c, d*) reaching down to the bottom of the bottle. The tubes *c* and *d* are connected with an elastic tube; another such tube connects either *a* or *b* with the absorbing-apparatus. One of the bottles, say I., is placed so that its bottom is raised above the top of II. If now *b* is connected with the absorbing-apparatus, and the air is sucked from *a* for a moment,

Fig. 311.



the siphon formed by *c, d* and the elastic tube begins to run, gas being aspirated from *b*. When the contents of I. are run out, the elastic tube is detached from *b*, the position of the bottles is reversed so that II. now stands higher, and the elastic tube is put upon *a*; the connection between *c* and *d* is not touched. Usually the siphon begins to act again of its own accord; otherwise it is started by sucking for a moment at *a*. The quantity of water running out of the bottles at each turn is determined once for all.

The plan just described has the drawback of requiring an attendant to change the position of the bottles, and is hence hardly convenient enough for continuous testing. For this purpose, if a meter is to be dispensed with, a vessel of large capacity, say several cubic feet, should be provided, sufficient to serve for 24 hours without special attendance. Such a vessel can be made of glass, stoneware, or wood lined with lead; it should be cylindrical and provided with a gauge for measuring the height of the water within; in order to act quite equally it should be on the principle of a Mariotte's bottle, as described on p. 517. The form adopted by Younger (J. Soc. Chem. Ind. 1887, p. 347) has no special advantages.

An excellent apparatus has been described by W. G. Strype (Trans. Newc. Chem. Soc. 1880, vol. iv. p. 357). We will here give a description of it, abridged from the inventor's own words, with two drawings, figs. 312 and 313, showing it in two different conditions; but it is unnecessary to say that some details, such as the absorbing-apparatus, may be varied without any detriment to the principle.

Fig. 312 shows it in the process of being charged with water and having the old solution removed; and in fig. 313 it is shown as in ordinary work. The measuring-vessel E is of some 5 cubic feet capacity. The supply of water to charge this vessel is through the cock A, communicating with the vessel by means of the large pipe B, C, which is carried up to the open end at D, and to such a height as to ensure that too much pressure is not thrown on the apparatus when it is being charged; if too much, of course the water will overflow at the open end D. The air or residual gas remaining in the measuring-vessel after each period of absorption escapes, when it is being refilled, through the tube $a\ a'\ a''$ into the lower vessel F, under the pressure of a small head of water of

Fig. 312.

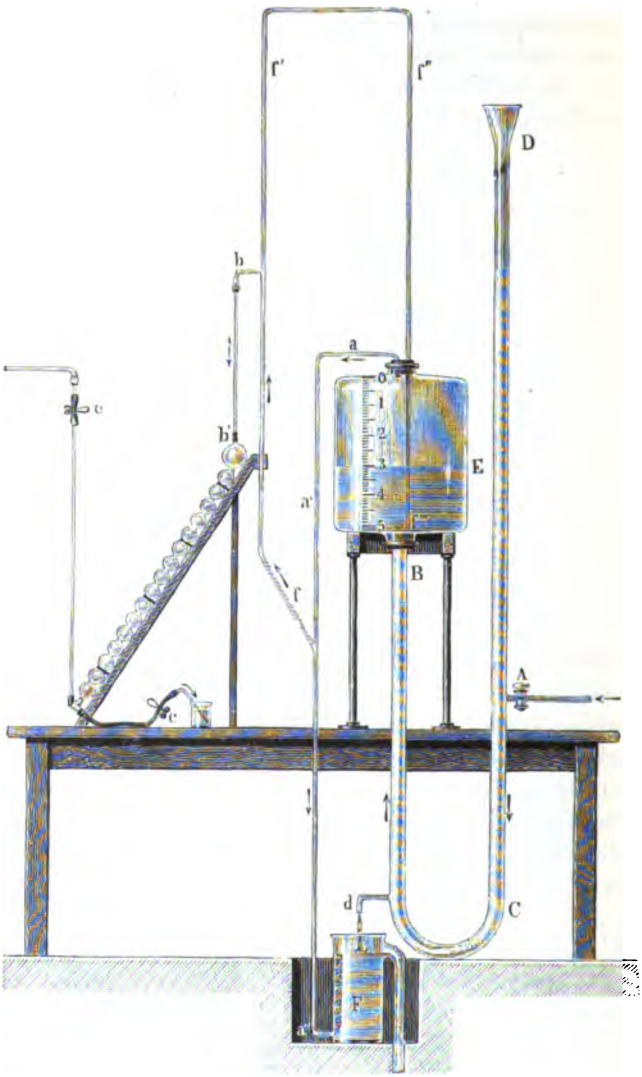
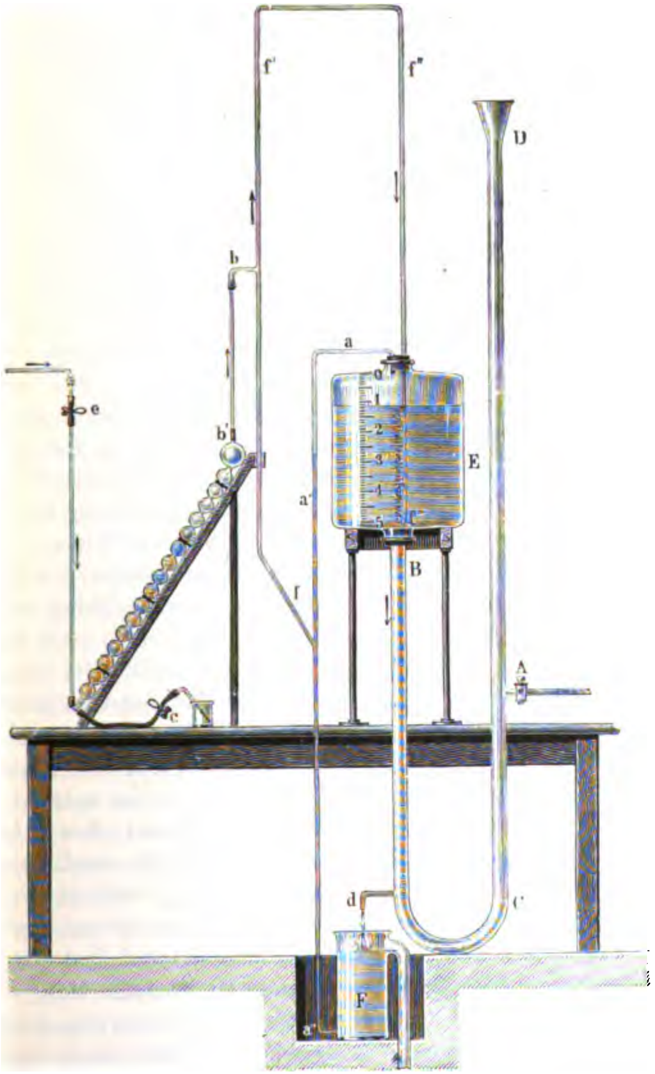


Fig. 313.



about one foot, and as the escaping air communicates by means of the tube *f b b′* with the test-bulbs, the pinch-cock at *c* being opened, the small pressure thus expels the old absorbing-solution as shown in fig. 312. When the vessel E is full, the old absorbing-solution being driven out of the bulbs, the cock A is shut, and the excessive water drains away from the small drip-pipe *d*, thus emptying all the connections to the condition shown in fig. 312; and the pinch-cock at *c*, and also the regulating pinch-cock on the pipe at *e*, which communicates with the chamber-exit, being closed, the flow ceases, and equilibrium is established by the apparatus being under the small vacuum due to the head of water in the vessel E over the open drip-pipe *d*. The pinch-cock *c* is now opened, and the india-rubber tube hanging from it is dipped into a beaker containing the test solution, which is now drawn up into the bulbs by the vacuum. When the charge is complete the pinch-cock at *c* is closed, and the regulating pinch-cock *e* opened to the required extent so as to admit the escaping gases from the chamber-exit to enter the apparatus; and absorption of the acids follows, together with accurate measurement of the volume dealt with; the residual gas passes into the measuring-vessel through the tubes *b′ b*, *f′ f″ f‴*. The latter tube is carried down at *f‴* close to the bottom of the vessel E, in order to secure a uniform flow of gas with the varying head due to the gradually diminishing level of water in the vessel, in the manner too well known to need further reference, and it is to secure this point that a difficulty arises in arranging such an apparatus. The tube *a a′ a″* must be sealed off when the apparatus is at work if the flow of escape through the absorbing-solution is to be at a uniform rate, and this is accomplished by a very simple plan. Upon turning on the water at A to charge the apparatus, the water runs down *a a′*, and when as low as the inclined pipe at *f*, air glides upwards, and the small quantity of water in the inclined pipe *f* also drains away; without this contrivance there would be a small quantity of water driven over into the test-bulbs each time the apparatus was charged, but the tube being placed in a diagonal direction entirely prevents this.

The proportions and relative positions of the various parts are accurately shown to scale in the drawings, and it is important this should be carefully attended to in constructing the apparatus.

The arrangement to contain the absorbing-solution consists of a series of 30 bulbs, each about 1⅛ inch diameter, with small and short necks between them: the bulbs are made in sets of 10 each; three sets are coupled together with small pieces of india-rubber tubing, and the charge of 300 c.c. occupies about 22 of them, leaving a little free space in the upper part of each. A large bulb of some 4 inches diameter is placed, as shown, at the head of the bulbs, to catch any of the absorbing-solution in case it should be drawn up through all the smaller bulbs by accidentally turning on the flow of gas with too much violence in starting the apparatus. The solution used in this way contains 100 c.c. normal caustic soda, diluted to 300 c.c. coloured with litmus*. The drain-pipe *d* is always open and is of small aperture, but sufficient to more than carry away the water as it drains from the measuring-vessel in ordinary working, and thus a constant vacuum is maintained.

The apparatus is preferably constructed of glass, with india-rubber junctions; but of course it can just as well be made with an iron or lead measuring-vessel and lead pipes, a water-gauge being employed to observe the level of the water in E.

The staunchness of all the parts is ascertained, when the apparatus has just been charged, by shutting off the pinch-cocks *c* and *e*, and seeing that no water drains from the open pipe *d*. In charging, the water freely flows from *d*, but the aperture being small this does not appreciably interfere with the filling of the vessel E.

Whatever be the system of aspirating the gases, they must be passed through certain *solutions to absorb the acids* contained therein as completely as possible. The different acid compounds of sulphur are estimated together, as well as those of nitrogen, whatever degree of oxidation they may possess. The following *prescriptions* agree in the main with those worked out by Hurter and published *by the British Alkali Makers' Association* in 1878; they are recorded in Lunge and Hurter's 'Alkali Maker's Pocket-book,' 2nd edition, pp. 118, 119. A continuous test over 24 hours is taken of the gases escaping from the exit-pipes of the Gay-Lussac towers, aspirating at least one cubic foot per hour by means of any aspirator acting at a constant rate, and recording

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* Methyl-orange should *not* be used in this case, as it is destroyed by the nitrous acid present.

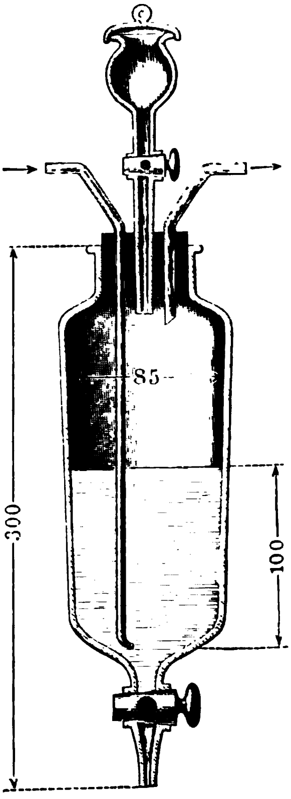

Fig. 314.

the volume of gas (=V) by means of gauging the aspirator or by a gas-meter. The volume V is reduced to 0° C. and 760 mm. pressure (=32° F. and 29·92 inches) by the tables contained in the 'Pocket-book,' pp. 28 *et seq.*[*], and is now called V'. In order to allow comparisons, the number of cubic feet of chamber-space per pound of sulphur burnt and passing into the chambers is recorded, excluding towers, but including tunnels, the amount of sulphur being taken by the weekly average, stating the distance of the testing-hole from the point at which the gases leave the Gay-Lussac towers. The absorption-apparatus consists of four bottles or tubes (fig. 314[†]), containing each not less than 100 c.c. of absorbing-liquid, with a depth of at least 3 in. in each bottle, the aperture of inlet-tubes not to exceed $\frac{1}{50}$ inch in diameter and to be measured by a standard wire. The first three bottles contain each 100 c.c. of normal caustic-soda solution (31 grams per litre), the fourth 100 c.c. distilled water. The caustic soda must be free from nitrogen acids. The gases are tested (1) for total acidity, stated in grains of SO_3 per cubic foot of gas, or else in grams per cubic metre; (2) sulphur acids; (3) nitrogen acids—both stated in grains of S and N per cubic foot (or grams per cubic metre). The analysis is carried out as follows:—The contents of the four bottles are combined, taking care not to unnecessarily augment the bulk of the liquids, and are divided into three equal parts, one of which is reserved for accidents &c. The first part is titrated with normal sulphuric acid (49 grams H_2SO_4 per litre) to ascertain total acidity. The number of c.c. of acid necessary for neutralization is called x. The second part of the liquid is gradually poured into a warm solution of potassium permanganate, strongly acidified with pure sulphuric acid. A small excess of permanganate must be present, and must be afterwards reduced by the addition of a few drops of sulphurous-acid solution, until only a faint red tint is visible. Now all nitrogen acids are present as HNO_3, but no excess of SO_2. The HNO_3 is estimated by its action on $FeSO_4$. 25 c.c. of a solution, containing per litre 100 grms. of crystallized ferrous sulphate and 100 grms. pure sulphuric acid, are put into a flask, 20 to 25 c.c. pure concentrated sulphuric acid is added, the mixture is allowed to cool, and the other mixture, treated with permanganate &c., is added. The flask is closed by a cork with glass tubes. A current of CO_2 passes through and issues beneath the surface of some water, to prevent entrance of air. First, all the air is expelled in this way by an apparatus evolving CO_2 by constant action; then the solutions are introduced, and the contents of the flask are heated to boiling, till the dark colour produced by the formation of NO has changed to a clear light yellow. This lasts a quarter of an hour to one hour, according to the quantity of HNO_3 present and that of the sulphuric acid added. The unoxidized ferrous sulphate is titrated by a semi-normal permanganate solution (yielding 0·004 grm. oxygen per c.c.); the c.c. used $=y$. Since the titre of the iron solution changes pretty quickly, it should be tested daily by taking out 25 c.c. with the same pipette as serves for the above-described operation, and ascertaining the amount of permanganate required for oxidizing it, $=z$ c.c. The magnitudes sought are found by the following equations:—

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[*] The law prescribes the cubic foot to be measured at 60° F. and 30 inches, which necessitates the use of other tables or factors than those mentioned in the text, but the difference is hardly perceptible, and is within the limits of experimental error.

[†] Taken from Jurisch, 'Schwefelsäurefabrikation.' p. 224.

1. *Total Acidity* in grams per cubic metre:

$$SO_3=\frac{0{\cdot}120(100-x)}{V'}.$$

2. *Sulphur* in grams per cubic metre:

$$S=\frac{0{\cdot}008(600-6x-z+y)}{V'}.$$

1. *Total acidity* in grains pe cubic foot:

$$SO_3=\frac{1{\cdot}852(100-x)}{V'}.$$

2. *Sulphur* in grains per cubic foot:

$$S=\frac{0{\cdot}12346(600-6x-z+y)}{V'}.$$

3. *Nitrogen* in grams per cubic metre:

$$N = \frac{0{\cdot}007(z-y)}{V'}.$$

3. *Nitrogen* in grains per cubic foot:

$$N = \frac{0{\cdot}10803(z-y)}{V'}.$$

If the nitrogen acids are not to be separately estimated (and the Alkali Act does not require this to be done), the above prescriptions can be extremely simplified. It is only necessary to employ the apparatus shown on p. 413, fig. 137, and intended for testing the burner-gases for sulphur acids, or else one of the absorbing-apparatus to be mentioned below is employed. The apparatus is charged with 100 c.c. of normal caustic-soda solution, coloured with phenolphthalein, which acts equally upon SO_2 and H_2SO_4, and this is re-titrated with standard acid. The caustic-soda solution should be as free as possible from carbonate, as CO_2 acts upon phenolphthalein as well. The formula for calculation is then No. 1 divided by 3, that is:—

$$SO_3 = \frac{0{\cdot}040(100-x)}{V'} \text{ grms. per cubic metre,}$$

$$= \frac{0{\cdot}617(100-x)}{V'} \text{ grains per cubic foot.}$$

When the object of testing the exit-gases is merely to ascertain the total acidity, in view of the requirements of the law (p. 736), it is sufficient to pass a certain volume of the gas through a solution of hydrogen peroxide, which oxidizes the SO_2 to H_2SO_4, and then to titrate all the acids, together with caustic soda solution and methyl-orange, and calculate them as SO_3. In a very exhaustive paper (Journ. Soc. Chem. Ind. 1902, p. 1490) R. F. Carpenter and Linder prove that the best way of proceeding is to employ for the absorption a mixture of 1 vol. semi-normal caustic-soda solution and 10 vols. hydrogen peroxide solution, which is afterwards re-titrated by phenolphthalein at a boiling heat, or by methyl-orange in the cold. In this case the nitrogen acids proper are also absorbed, but NO is only very little acted upon.

The *shape of the absorbing-vessels* is not at all indifferent. When employing ordinary bottles with simple glass tubes dipping below the liquid, the absorption is often incomplete, even if several bottles are used in succession, which causes considerable pressure. The use of very narrow inlet-tubes, as prescribed in the 'Alkali Maker's Instructions' (see above, p. 744), lessens, but does not entirely avoid the evil, of incomplete absorption. The potash-bulbs used in organic analysis cannot be employed, because it is too difficult to empty their contents without any loss.

Fig. 315.

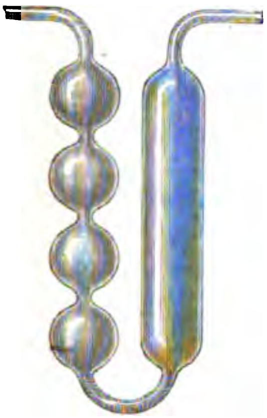


Fig. 316.

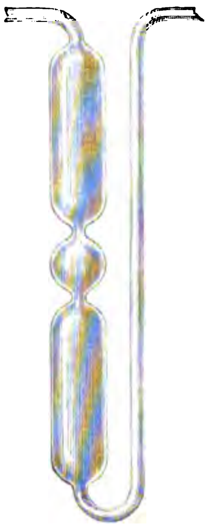


Fig. 317.

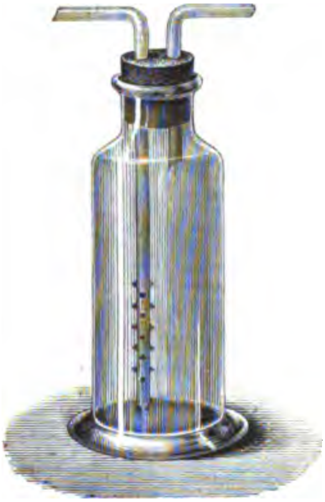
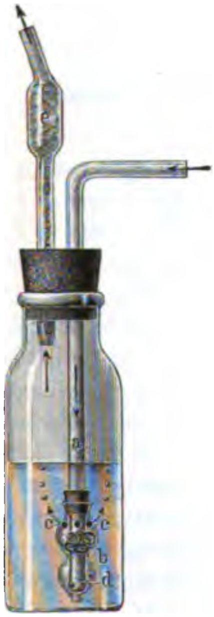


Fig. 318.



The absorption is better when using Mitscherlich's tubes (fig. 315), of which Todd's tubes (fig. 316) are but a slight modification. The shape of absorbing-bottle shown in fig. 317 serves also very well. Better than these is the Pettenkofer tube as modified by myself (fig. 319) and still better a 10- or 15-bulb-tube, as shown in fig. 320, one of which generally suffices for complete absorption.

Ordinary absorbing-bottles fail of their purpose where white mists of acid in a vesicular form have to be dealt with, as in the case of the gases from overhead-fired pans or beaker-apparatus for rectified vitriol (comp. Chapter IX.). In these cases the bottles may be shaken a hundred times and upwards without entirely removing the white mist. The Alkali Inspectors have, however, elaborated a bottle performing this service most efficiently. It is shown in fig. 318, where we notice the absorbing-bulb, containing inside a number of india-rubber rings (cut from ordinary small tubing). The gases pass through the central tube *a*, by small holes *d* near its closed end, into the bulb *b*, and before they issue through the holes *c c* they are broken up into small bubbles by the india-rubber dippings, which are washed by the movement of the liquid in the apparatus, and thus produce a thorough scrubbing of the gas. The upper bulb is ¾-inch wide, the lower ⅝-inch, the bottom-opening ¼-inch; these proportions should be observed to attain the object. Exit-tube *e* is filled with glass-wool.

Nitric oxide can be (and generally is) present in the gases after passing through the absorbing-bottles. It can be estimated in an absorbing-tube (fig. 319), or better in a bulb-tube (fig. 320), interposed between the tubes of the apparatus serving for estimating the acids and the aspirator. The bulb-tube is charged with 30 c.c. of seminormal permanganate solution and several c.c. of sulphuric acid. The gas is passed through for 24 hours, and the tube emptied and washed out. Now add 50 c.c. of ferrous-sulphate solution, corresponding to $2x$ permanganate

Fig. 319.

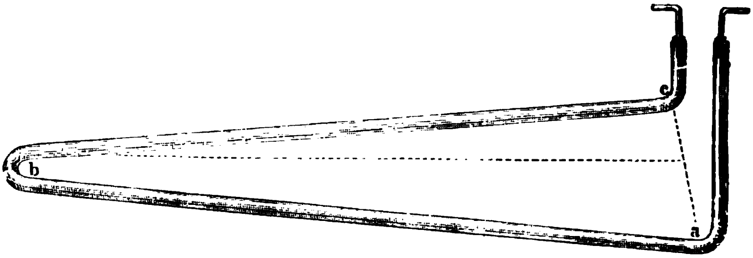
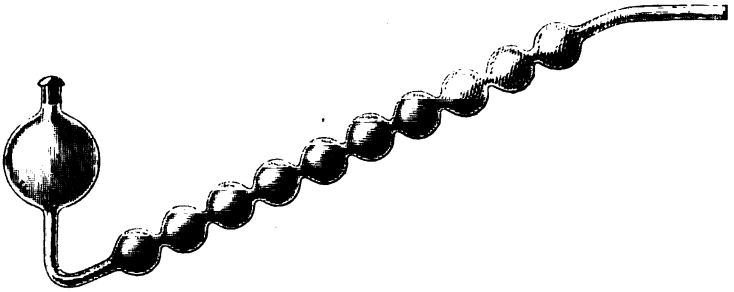


Fig. 320.



(comp. p. 745), and re-titrate the decolorized liquid with permanganate. (If a precipitate of manganese peroxide has been formed in the absorbing-tubes, rinse the tubes with some of the iron solution.) The quantity of the permanganate last used is called u. The NO has altogether consumed $(30+u-2z)$ c.c. of permanganate, giving :—

In grams of nitrogen per cubic metre of the volume V'.	In grains of nitrogen per cubic foot.
$N=\frac{0{\cdot}007\,(30+u-2z)}{3V'}$	$N=\frac{0{\cdot}10803\,(30+u-2z)}{3V'}$.

The quantity of nitric oxide present in chamber exit-gases may be at times rather considerable without attracting notice, as it oxidizes only very slowly when strongly diluted with inert gases. This makes some of the absorbents proposed, as hydrogen peroxide or a mixture of strong sulphuric with nitric acid, practically useless, as proved by myself by many laboratory experiments. The paper of Carpenter & Linder, quoted p. 746, corroborates this. Just for this reason I first proposed in 1881 the use of an acid solution of potassium permanganate and the apparatus described here. Even this process requires a very good absorbing-apparatus and a very slow stream in order to take all the NO out of the gases.

The apparatus and methods described by Lovett (J. Soc. Chem. Ind. 1882, p. 210) may be consulted by those specially interested in this subject, but call for no special remark here. This holds good also of the papers of G. E. Davis (Chem. News, vol. xli. p. 188) and Pringle (J. Soc. Chem. Ind. 1883, p. 58).

The gas collecting in the aspirating-vessel of any of the above-described apparatus, being an average sample of the exit-gases free from acids, is very conveniently employed, in preference to samples taken at random over the day, for *estimating the oxygen* contained in the exit-air. This estimation has been previously described (p. 417), and we have here only to show how the estimation of oxygen in the exit-gas may be used for *ascertaining the quantity of sulphur burnt,* expressed in grams per litre of the exit-gas, so that the quantity of sulphur lost in that gas may be put in direct comparison with the total sulphur used. For this the following formula has been proposed by me in Dingler's Journal, vol. 226, p. 634 :—

$$(20{\cdot}95-a)\times 0{\cdot}009637\times\frac{1}{1{\cdot}00367\,t}\times\frac{h}{760}=x.$$

Here a denotes the percentage of oxygen in the exit-gas, t its temperature, h the barometrical pressure in millimetres, x the total quantity of the sulphur actually burnt, expressed in grams per litre of the exit-gas; with this the quantity actually found should be compared, in order to find the percentage of loss. It should not be overlooked that no account is here taken of the sulphur remaining in the cinders.

Theory of the Formation of Sulphuric Acid in the Lead Chambers.

When describing in previous Chapters the behaviour of sulphur dioxide towards the various nitrogen compounds in the presence of water, sulphuric acid, &c., and the formation and decomposition of nitrososulphuric acid, we have been obliged repeatedly to forestall theoretical considerations; but these will now be brought forward connectedly and in detail.

We must from the commencement bear in mind the fact that during the burning of sulphur, whether in the form of brimstone, pyrites, or blende, &c., substantially sulphur dioxide (SO_2) alone is formed; the formation of sulphuric anhydride or acid, always occurring at the same time (at least in the case of pyrites), is not taken into account here, being merely a secondary reaction, and not exempting us from the task of explaining the oxidation of the sulphur dioxide in the lead chambers. That this does not take place to an appreciable extent by the direct action of the atmospheric oxygen, may at the outset be taken as established. But it is just as certain that the oxygen of the nitre introduced into the process does not suffice to account for it; for the sulphur dioxide from 100 parts of sulphur requires another 50 parts of oxygen in order to be oxidized to sulphuric acid, which would correspond to 81·5 parts of nitrate of soda, even if this compound were reduced to nitrogen. But it is well known that, under favourable conditions, only $\frac{1}{30}$ to $\frac{1}{25}$ of the above quantity of nitre is used; and this fact must now be explained.

The first theory on this subject was propounded as early as 1806, by Clément and Désormes (' Annales de Chimie,' lix. p. 329); and it must be owned that they had observed most of the essential facts, and connected them by a theory which has not had to be entirely abolished, but only to be modified with the growth of our knowledge. They had studied the behaviour of sulphur dioxide towards a mixture of nitric acid and atmospheric air; and they proved that, even in the crude process then in use (where a mixture of brimstone, saltpetre, and moist clay was heated in a furnace and the gaseous products were conducted into the lead chamber), considerably more oxygen was transferred to the sulphur dioxide than the saltpetre contained. They already explained this fact in substantially the same way as it is explained now-a-days, viz. thus:—From the nitre-gas oxidized by atmospheric oxygen, and from the sulphur dioxide, sulphuric acid is generated, whilst the nitre-gas is re-formed. The nitric acid is only the instrument for the complete oxidation of the sulphur, which in doing its work is not destroyed; for its "basis," the nitre-gas takes up oxygen from the atmospheric air in order to present it to the sulphur dioxide in a suitable state; but it remains in its original state at the end of the process of forming the sulphuric acid. The presence of water they explain as necessary, first, for keeping the temperature of the reaction sufficiently low; secondly, for condensing the sulphuric acid as it forms. They also observed in the process the production of white star-shaped crystals, which on contact with water gave out nitre-gas with a strong evolution of heat, and they already suspected that this compound had a prominent share in the acid-forming process.

H. Davy showed, in 1812, that the presence of water is absolutely necessary (Berzelius, 'Lehrbuch,' i. p. 471), because in the dry state the gases do not react upon each other; but a small quantity of water added to the mixture of sulphur dioxide and nitrous vapours causes the formation of the crystals observed by Clément and Désormes. Davy, therefore, considered that body an intermediate link indispensable for the formation of sulphuric acid; with our present notation we should express his opinion in this way:—

$$
\begin{array}{rll}
\text{I.} & 2\,SO_2+3NO_2 & +H_2O=2\,SO_2(OH)(ONO)+NO\,; \\
\text{II.} & 2\,SO_2(OH)(ONO) & +H_2O=2\,SO_2(OH)_2+NO_2+NO\,; \\
\text{III.} & 2\,NO+2O & =2\,NO_2.
\end{array}
$$

Therefore we commence with 3 NO_2; and we recover of this 1 NO_2 in the equation II., 2 NO_2 in the equation III., in order to begin the process over again.

This opinion has been accepted by many other chemists, for instance La Prévostaye (Ann. de Chim. et de Phys. lxxiii. p. 326). Gmelin also adopts it; he says ('Handbuch,' 5th ed. i. p. 875) :—"In all these cases there are mixed in the chamber sulphurous acid gas, vapour of hyponitric acid, arising from the nitric-oxide gas and from the oxygen of the air, and aqueous vapour, which is introduced on purpose. There is a crystalline compound of sulphate of nitric oxide with oil of vitriol formed, which sinks down to the bottom of the lead chamber in the shape of a thick white mist and dissolves in the water present there and forms dilute sulphuric acid, nitric-oxide gas being evolved. This nitric-oxide gas, with the remaining oxygen of the air, again forms vapour of hyponitric acid, which condenses a fresh quantity of sulphurous acid gas into the crystalline compound, and so forth."

An *apparently* simpler explanation of the vitriol-chamber process was given by Berzelius ('Lehrbuch der Chemie,' Woehler's translation, 4th ed. 1835, vol. ii. p. 12). He believes the formation of chamber-crystals to be not a necessary intermediate process, but only an exceptional case happening in some parts of the chamber where steam is wanting. The process proper, according to him, consists of the transference of oxygen from "nitrous acid" to sulphur dioxide (and water), producing sulphuric acid and nitric oxide, from which, by means of oxygen, nitrous acid is regenerated.

We should therefore have to express the process in our present notation by the following equations :—

$$(1)\ SO_2+N_2O_3+H_2O=H_2SO_4+2\,NO\,;$$
$$(2)\ 2\,NO+O=N_2O_3.$$

But I have shown (Ber. d. deutsch. chem. Ges. 1888, p. 3225) that Berzelius, as was natural in those days, made no sharp distinction between N_2O_3 and N_2O_4, and evidently by "nitrous acid" often means N_2O_4. It is also an important fact that in his 'Jahresbericht' for 1844, when the difference between N_2O_3 and N_2O_4 had become clearer, he distinctly states (p. 62) that N_2O_4 is formed when NO meets a sufficient quantity of oxygen or atmospheric air, whilst with an excess of NO, that is, in case of a deficiency of oxygen, N_2O_3 is formed, together with some N_2O_4. In fact most subsequent writers have not introduced nitrous andydride, but *nitrogen peroxide* into the explanation of the chamber-process, starting from the indubitable fact that in ordinary laboratory experiments nitric oxide with an excess of oxygen forms almost entirely, or perhaps even exclusively, nitrogen peroxide, and tacitly assuming (without any proof of ever having attempted to detect its presence) that nitrogen peroxide was the oxide of nitrogen prevailing in vitriol-chambers; also overlooking that the above-mentioned laboratory fact is entirely modified by the presence of other substances in the vitriol-chamber. Thus it came to pass that the following equations were generally held to express the vitriol-chamber process:—

$$(3)\ SO_2+NO_2+H_2O=H_2SO_4+NO;$$
$$(4)\ NO+O\qquad =NO_2^*.$$

The great simplicity of this expression seemed to be its recommendation, but it was overlooked that in nature the simplest explanation is very often *not* the expression of truth.

Even long after Berzelius no sharp distinction was made between the equations (1)+(2) and (3)+(4); probably most chemists tacitly assumed, as was explicitly done by some, that the vitriol-chambers contained a mixture of N_2O_3 and N_2O_4, both of which acted as oxygen carriers upon SO_2, and this was generally meant when speaking of the "theory of Berzelius," which was certainly accepted by very many chemists.

For some time another theory, that of Peligot, published in 1844 (Annales de Chim. et de Phys. (3) xii. p. 263), contested the palm with it, and was accepted, more especially in France, until very recently; even Kolb ('Études sur la Fabrication de l'Acide sulfurique,' Lille, 1865, p. 22) adhered to it; and so did Pelouze and Frémy ('Traité de Chimie,' 2nd edition, i. p. 398).

Peligot, like Berzelius, denied that the chamber-crystals had an essential share in the formation of sulphuric acid, or that they appeared at all in the regular process, either in a solid form or in solution. He attributes the oxidation of the sulphur dioxide within the lead chamber exclusively to nitric acid, not to the lower oxides of nitrogen. The water is added to decompose the hyponitric acid formed from nitric oxide and atmospheric oxygen, or the nitrous acid formed at the same time, into nitric oxide and [hydrated] nitric acid, and thus to regenerate the only oxidizing agent acting in this process, viz. nitric acid. In watery solution, he says, no nitrous acid exists [which is altogether wrong]; from a mixture of nitric oxide and atmospheric air not N_2O_3, but only N_2O_4 is formed. These opinions will be made clearer by the following equations (rendered into modern symbols):—

---

* Here, as in all other instances, we shall use the symbols N_2O_4 and NO_2 as interchangeable according to convenience of expression.

$$\begin{array}{rll} \text{I.} & SO_2+2NO_2\,.\,OH & =SO_2(OH)_2+N_2O_4; \\ \text{II.} & 2N_2O_4+H_2O & =N_2O_3+2NO_2\,.\,OH; \\ \text{III.} & 3N_2O_3+H_2O & =4NO+2NO_2\,.\,OH; \\ \text{IV.} & 2NO+2O & =N_2O_4. \end{array}$$

The experiments upon which Peligot founded his theory certainly proved that *concentrated* nitric acid oxidizes sulphur dioxide even at the ordinary temperature, nitrogen peroxide being formed. But sulphur dioxide acts with more difficulty on dilute nitric acid, and only with the aid of heat, nitric oxide being formed. Weber points out that Peligot's experiments do *not* prove that nitric acid of that degree of dilution which, according to his own theory, must exist in the lead chambers, at the temperature prevailing there, is really decomposed by sulphur dioxide. On the contrary, according to Weber's observations, nitric acid of 2 per cent. is not at all changed when cold by sulphur dioxide; there is no appreciable action below 80° C., a temperature which, in normal work, is not prevalent in the lead chambers.

The researches of R. Weber in 1866 and 1867 (Poggendorff's 'Annalen,' cxxvii. p. 543, and cxxx. p. 329) have proved the complete futility, in all respects, of Peligot's theory, and have greatly contributed towards elucidating the process within the lead chamber. Briefly, he states as follows*:—In the chambers, to 100 parts of sulphur, 220 parts of water are used, and from 6 to 8 parts, at most, of nitrate of soda. According to Peligot's equations the liquid at the bottom of the chamber could thus only contain from 2 to 2·3 per cent. of N_2O_5, even without taking into account that, according to him, one-third of the nitrogen passes as NO into the atmosphere of the chamber: $3\,N_2O_4=2\,N_2O_5+2\,NO$. [Properly speaking, therefore, only 1·6 to 1·8 per cent.

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* Some parts of Weber's as well as of Winkler's work have been noticed in Chapt. III. p. 212 *et seq.*

of N_2O_5 could be present in the chamber-acid.] Weber found, by direct experiments, when sulphur dioxide was conducted into nitric acid containing even a higher percentage (viz. 3 per cent.) of N_2O_5, that, at the ordinary temperature, after the lapse of half an hour no sulphuric acid at all had been formed, and extremely little at 40° C. (about the temperature of the chambers); whilst in the well-known laboratory experiment in a glass flask, from a mixture of SO_2, NO, atmospheric air, and water there is an easy and instantaneous formation of sulphuric acid; and the lead chambers also produce this acid so quickly that the extremely slow action of nitric acid cannot account for it at all. Furthermore, Weber proved that Peligot was mistaken in supposing that nitrogen peroxide with water merely decomposes to NO and NO_3H, and that nitrous acid cannot exist in presence of an excess of water; for water which has absorbed vapours of nitrogen peroxide liberates free iodine from a solution of potassium iodide, even when it has been heated to incipient ebullition; it must therefore contain nitrous acid, for neither pure nitric acid nor nitric oxide attacks potassium iodide.

Further, whilst dilute nitric acid has next to no action on sulphur dioxide at the ordinary temperature, there is a strong action between SO_2 and water which has absorbed the vapour of nitrogen peroxide, or if such water is added to the same dilute nitric acid which at first showed no action, or, more simply, if, instead of pure nitric acid, fuming nitric acid strongly diluted with water be used. *Accordingly, the nitrous acid generated by the contact of nitrogen peroxide and water oxidizes the sulphur dioxide much more readily than nitric acid does; nitrous acid is therefore undoubtedly the primary cause of the reaction for the formation of sulphuric acid when moist air meets sulphur dioxide and the vapour of nitrogen peroxide.* The nitric acid which is formed on the decomposition of N_2O_4 by water remains undecomposed by SO_2 *if much water is present.* Under certain circumstances, however, as will be shown below, the nitric acid is decomposed as well.

For the chamber-process the behaviour of N_2O_4 and N_2O_3 towards sulphuric acid of various degrees of dilution with water must also be taken into account, as those gases come into contact with such acids, both in the shape of minute drops suspended in the atmosphere of the chamber and in the stock collected at the bottom. According to their degree of dilution, the sulphuric acids contain nitrososulphuric acid (chamber-crystals), free N_2O_4, or N_2O_3, as has been explained in detail on p. 213 *et seq.*; but all these liquids, when their density is much higher than that of ordinary chamber-acid, are rapidly decomposed by sulphur dioxide, sulphuric acid being formed. The decomposition of the absorbed vapours by means of water, for the purpose of forming nitric acid, is therefore quite unnecessary and improbable; but the water must serve for forming the hydrate SO_4H_2, and therefore only in its presence can SO_2 be promptly oxidized by N_2O_3.

It is of importance in practice that moderately concentrated mixtures containing nitric acid are more easily decomposed by sulphur dioxide than highly concentrated ones. When nitrous acid is dissolved in the pure hydrate SO_4H_2, or even in ordinary vitriol of 170° Tw., sulphur dioxide does not act upon it at all, or at least very incompletely.

When nitric acid is mixed with *dilute* sulphuric acid of varying concentration, it is seen that in a mixture of pure nitric acid of 1·25 spec. gr. with sulphuric acid of 70° Tw. the nitric acid is not decomposed by sulphur dioxide in the cold, but quickly on being heated, with evolution of nitric oxide; in the case of stronger acids (from 77° Tw. upwards) the decomposition begins in the cold, and the liquid then contains nitrous acid. Evidently the sulphur dioxide first produces nitrous acid in those mixtures, which is proved by their colour and by their action on potassium iodide; and in the *second* stage the nitrous acid yields up oxygen direct to the sulphur dioxide, without being compelled, as Peligot assumed, to be redecomposed into nitric acid and nitric oxide—a preposterous assumption. Thus even dilute nitric acid, brought into contact with moderately strong sulphuric acid, may be useful for the chamber-process, as in that case it yields up its water to the sulphuric acid, and in the concentrated state it is readily attacked by sulphur dioxide; this is just what takes place in the chamber. Weber points out that Berzelius ('Jahresbericht,' xxv. p. 65) contradicted Peligot's opinion that, in the chambers, no nitrous acid is formed from nitric oxide and atmospheric air, but merely nitrogen peroxide; from eudiometric experiments with nitric oxide and oxygen he concluded that, according to the excess of one gas or the other, there is more or less condensation, and that in any case there is always a formation of nitrous acid, even with an excess of oxygen (comp., however, p. 761).

According to the above reasoning, the water cannot play the part which Peligot's theory attributes to it as the essential one, viz. that of decomposing N_2O_4 and N_2O_3, and causing the formation of nitric acid. The water no doubt acts chiefly by making possible the formation of sulphuric acid proper (SO_4H_2). With the modern opinions on the essence of acids this is a matter of course; and it is therefore unnecessary to cite the many experiments and arguments adduced by Weber as proof that the water disposes the sulphur dioxide to oxidation. It should, however, be added at once that a quantity of water just corresponding to the formula SO_4H_2 is not sufficient, because this strong acid would dissolve the nitrous gas, so as to form nitrososulphuric acid, and would thus withdraw it from the chamber-process; sufficient water must be used to decompose the nitrososulphuric acid and to form an acid of no more than 124° or 128° Tw.; then only does the chamber-process go on regularly, as we shall see later on.

According to Weber's theory, the following process, therefore, takes place within the chambers:—The sulphur dioxide is oxidized, mainly by the oxygen of the nitrous acid, which thereby passes into nitric oxide; it does this, however, only when dissolved in water or in dilute sulphuric acid; and such a watery solution is formed either direct from free N_2O_3 or by the decomposition of N_2O_4. In the latter case, at the same time, nitric acid is formed, which can only be decomposed by the mediation of already formed sulphuric acid. The part played by the water has just been explained.

There is an agreement in many, but not in all, points between the opinions of Weber and those published almost simultaneously by Cl. Winkler (Untersuchungen &c. p. 20). Winkler also affirms the oxidation of sulphur dioxide by nitrous acid; but according to him the part played by nitrogen peroxide is more essential than that which Weber assigns to it. Winkler believes the latter to be formed principally by the action of air on nitric oxide; it then combines with sulphur dioxide and water to form nitrososulphuric acid, which sinks to the bottom in the shape of the well-known mist, here comes into contact with the dilute hot chamber-acid and dissolves in it, evolving gaseous N_2O_3, which oxidizes a fresh quantity of sulphurous acid, thereby passing into NO, the latter beginning the process anew.

The fact that Weber points chiefly to N_2O_3, Winkler principally to N_2O_4 as the active agents in the chamber-process does not form a very essential difference in their views, as neither of them assumes either one of these oxides to be formed exclusive of the other. A more fundamental difference is this, that Weber, like Berzelius, does not admit the intermediate formation of nitrososulphuric acid as an essential feature of the process, whilst Winkler does so, thus reverting to Davy's theory, which he merely develops in the light of modern knowledge and more especially of his own investigations.

Formerly some writers objected to the theories hitherto stated that there is a difficulty in assuming a simultaneous oxidation of nitric oxide and reduction of higher oxides to NO. But this objection cannot be held as valid, and it would apply to any other theory ever brought forward for the chamber-process, or, for that matter, for any other process where an "intermedium" or "carrier" comes into play, and what would now be called a "pseudocatalytic" process (see below). Although both processes undoubtedly take place at the same time, this may happen in the same chamber under different conditions: when in a certain part nitrous gas is reduced to nitric oxide, sulphur dioxide vanishes at that part, and the excess of oxygen present everywhere can now oxidize the nitric oxide again; by currents, diffusion, &c. fresh sulphur dioxide is brought in, and the process commences again. Besides, in any case the law of the action of masses comes into play in that part of the process where reversible reactions take place, *i. e.* the decomposition of nitrososulphuric acid by water, as we shall see later on.

When, in 1878, the first edition of this work was written, the question had not practically advanced beyond the labours of Weber and Winkler, both of whom relied on laboratory experiments, not on researches made with actually working vitriol-chambers. The composition of the gases in normally or irregularly working chambers was not even known. The colour of the gases precluded the assumption that NO was the pravailing oxide of nitrogen, except perhaps in the first part of the system; it was also known that nitric acid did not make its appearance except under very irregular conditions. But the choice still lay between N_2O_3 and N_2O_4 as the prevailing constituent of the "nitrous vapours" in the vitriol-chamber, and it was not known which of these might be the real oxygen carrier. I myself at that time thought I had good reasons for assuming that in a *normally* working chamber, where there is neither too much nor too little oxygen, the nitrous acid greatly predominates over the nitrogen peroxide. This I inferred, 1st, because according to Winkler's and my own experiments nitric oxide in the presence of sulphuric acid of moderate strength, which is everywhere present in the chamber in the shape of a mist, is not oxidized beyond N_2O_3 even by an excess of oxygen; 2nd, because the nitrous vitriols analyzed by me never showed more than traces of higher oxides than N_2O_3 (that is, nitrososulphuric acid proper), whilst, for instance, when the pure nitrogen peroxide given off by heating lead nitrate was absorbed by sulphuric acid, a mixture of one molecule of N_2O_3 (in the shape of nitrososulphuric acid) and two of HNO_3 was always formed. The different results obtained by several chemists (Kolb, Winkler, Hurter) with respect to their nitrous vitriols I referred to faulty analytical methods or else to irregular work. Where the formation of sulphuric acid ceases almost entirely in the last chamber, the condition for forming nothing but N_2O_3 is absent; and in that case first N_2O_4, and then, by its contact with water, also HNO_3 will be formed. If, however, the free oxygen should be too much diminished, the sulphur dioxide, then in excess, will at once reduce N_2O_3 and N_2O_4 to NO, and the chamber will turn pale. The same will happen when too much air enters, because then the gas gets too much diluted. When there is a deficiency of sulphur dioxide (which in normal work ought not to happen), much of the nitrogen oxides will be converted by the oxygen in excess to N_2O_4, which will be split up with the water into $N_2O_3 + NO_2 . OH$. This, however, can only happen when the chamber-acid is very dilute; otherwise from the first only N_2O_3 is formed (see above), and therefore no $NO_2 . OH$ will appear. (This is a succinct summary of my opinions, as held at the time when the first edition of this work appeared, on the strength of Weber's and Winkler's experimental researches.)

A solid basis for a true theory of the vitriol-chamber process could only be formed by investigating the manufacturing process itself in all its stages, and, both as regards normal and irregular work, by an extended series of gas-analyses and other pertinent observations. The first and hitherto the only complete investigation of this kind was that made subsequently by myself in conjunction with Naef at the Uetikon works near Zürich, to which allusion has already been made (Chem. Ind. 1884, pp. 5–19). The results of this investigation have not been shaken by any others carried out since, so far as the facts of the case are concerned; but the explanations at that time given by myself and by other chemists have had to be modified considerably, especially in consequence of the further experimental work conducted by me in 1885 (J. Chem. Soc. xlvii. p. 465; Ber. d. deutsch. chem. Ges. xviii. p. 1384; comp. other work done before and after, mentioned Chap. III. p. 212 *et seq.*). I proved that in the *dry* state, and out of the reach of sulphuric acid, nitric oxide with an excess of oxygen combines to form nitrogen *peroxide* exclusively, or nearly so. If dry nitric oxide, being in excess, meets with an insufficient quantity of oxygen, a considerable amount of N_2O_3 is formed along with N_2O_4 (according to the view held at that time). In the presence of moisture, nitric oxide and excess of oxygen combine to form nothing but nitric acid. *Dilute* sulphuric acid (spec. grav. 1·405) acts on the whole like water, but a small quantity of nitrous acid is formed, as much as can exist in a stable solution in the acid (nitrososulphuric acid cannot exist in such dilute acid). Perhaps the most important observation, combined with others formerly made, was this:—If *strong* sulphuric acid is in presence of a large excess of oxygen, and nitric oxide is slowly passed into it, only that portion of NO which is in *immediate* contact with sulphuric acid, and so far as nitrososulphuric acid can be formed, is not oxidized beyond the state of N_2O_3 (as previously found by Winkler and myself); but all the gaseous molecules coming into contact with oxygen *outside* the acid, even immediately above it, behave like dry NO and excess of O generally—that is, they combine to form N_2O_4.

This last observation made it impossible to maintain, as had been done in the first edition of this work, and in some of my later papers, that the reason why NO and O within the vitriol-chambers do not combine to form N_2O_4, but merely N_2O_3, is found in the fact that there is a mist of sulphuric acid floating all over; for the liquid particles of sulphuric acid forming that mist are still at very great distances from one another relatively to the amount of molecules of NO and O present, and wherever the latter act upon one another otherwise than immediate absolute contact with the acid, they will not yield N_2O_3, but N_2O_4. Hence no theory can truly explain the vitriol-chamber process which presupposes the reduction of nitrous compounds to NO as a necessary step, for this would naturally lead to the formation of N_2O_4, and further on of HNO_3, neither of which occurs in a regularly working vitriol-chamber. It is true that Raschig (Ann. d. Chem. ccxlviii. p. 135) asserts that nitric oxide, even when meeting a very large excess of oxygen, is not converted into N_2O_4, but into N_2O_3, provided that the oxygen is diluted with nitrogen, as in atmospheric air. But this assertion, which is opposed to the statements of all other chemists, has been entirely disproved by my researches (Berl. Ber. 1888, p. 3234), which showed that Raschig's experiments were badly conducted, and that NO is transformed into nitrogen peroxide by atmospheric air just as well as by pure oxygen.

The whole of Raschig's arguments and hypotheses are vitiated by the recognition of the fact that nitrogen trioxide, N_2O_3, does not exist in the gaseous form except in traces, as we have shown before (p. 214). This makes it an absurdity to maintain, as he does, that NO with atmospheric air forms N_2O_3, not NO_2. Of course my own theory is also affected by the above fact. But, as I have shown in Chapter III. p. 214, that theory is altogether compatible with the light gained by more recent knowledge, since a mixture of $NO+NO_2$ behaves towards sulphuric acid exactly like N_2O_3.

Raschig's own theory of the vitriol-chamber process (Ann. Chem. ccxli. p. 242) is very curious. He assumes as an intermediary link the temporary formation of a compound which he calls "dihydroxylamine-sulphuric acid," of the formula $(OH)_2N SO_2OH$, but which nobody has seen, and whose preparation in the free state he himself does not expect to be possible. He assumes this compound to be formed when nitrous and sulphurous acid meet, but to be instantly decomposed with more nitrous acid into NO, SO_4H_2, and H_2O; NO is then again oxidized to nitrous acid, and the process begins anew. His equations are:

$$\begin{aligned}
&(a)\quad N(OH)_3+HSO_2OH &&=(OH)_2NSO_2OH+H_2O;\\
&(b)\quad (OH)_2NSO_2OH+N(OH)_3 &&=2\,NO+H_2SO_4+2\,H_2O;\\
&(c)\quad 2\,NO+O+3H_2O &&=2N(OH)_3.
\end{aligned}$$

I have shown (Ber. d. deutsch. chem. Ges. 1888, pp. 67 & 3223) how utterly unfounded are all the arguments adduced by Raschig for his view, evidently in ignorance of the actual working of vitriol-chambers and in neglect of the laboratory work of former chemists;

and we cannot waste our space here with repeating the refutation of a completely exploded theory *.

Several facts have to be reconciled in any true theory of the lead-chamber process: 1st, the fact that the chambers contain at first a mixture of more than 1 mol. NO to 1 mol. NO_2, later on almost exactly equal molecules of NO and NO_2, but in regular work never any excess of NO_2 over this proportion, which excess we have in our former discussions called "free" nitrogen peroxide (Lunge and Naef's observations at Uetikon); 2nd, that NO and an excess of O combine to form N_2O_4, and only where NO and O meet at the same time sulphuric acid of sufficient concentration they form nitrous acid, but not in the free state, merely in the shape of $SO_2(OH)(ONO)$; NO and O, in the presence of H_2O and SO_2, may also form directly $SO_2(OH)(ONO)$. A new theory of the chamber-process, based on these fundamental and all other observed facts, had been clearly, although very briefly, indicated by myself in my before-mentioned paper of 1885 (J. C. S. xlvii. p. 470), and it has been further developed in subsequent papers, especially Ber. d. deutsch. chem. Ges. 1888, pp. 67 & 3323.

The principal ideas of that theory were stated by me in 1885 as follows:—"*Sulphur dioxide combines directly with nitrogen trioxide, oxygen, and a little water to form nitrososulphuric acid, which floats in the chamber as a mist; on meeting an excess of water, equally floating about as a mist* [probably mostly or all in the shape of very dilute sulphuric acid], *the nitrososulphuric acid splits up into sulphuric acid, which sinks to the bottom, and nitrogen trixoide, which begins to act anew. Hence it is not, as hitherto generally assumed, the nitric oxide,* NO, *but the nitrogen trioxide,* N_2O_3, *which acts as carrier of oxygen in the vitriol-chamber process.*" As mentioned later on, the formation of sulphuric acid is not brought about by alternate *oxidation* of NO to N_2O_3 or N_2O_4, and subsequent *reduction* of these compounds to NO, but by a *condensation* of nitrous acid with sulphur dioxide and oxygen into nitrososulphuric acid, and a subsequent splitting up of this compound by an excess of water. [Nowadays this might be expressed as follows: the combination of sulphur dioxide, oxygen, and water to sulphuric acid is brought about by the pseudocatalytic action of nitrous anhydride.]

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* This is all the less necessary as Hamburger (J. Soc. Chem. Ind. 1889, p. 164) has given a summary of the controversy for English readers. Nor has Raschig since that time attempted to advance better arguments for his views, and it is all the stranger that some modern books take the trouble to devote some space and consideration to them, as if they were to be taken seriously.

The reactions here indicated are expressed by the equations:

$$(1)\quad 2SO_2+N_2O_3+O_2+H_2O = 2SO_2(OH)(ONO),$$

$$(2)\quad 2SO_2(OH)(ONO)+H_2O=2H_2SO_4+N_2O_3;$$

but they assume even a simpler shape, if, instead of nitrous anhydride, nitrous acid is introduced into the equations, thus:

$$(1a)\quad SO_2+NOOH+O = SO_2(OH)(ONO),$$

$$(2a)\quad SO_2(OH)(ONO)+H_2O=H_2SO_4+NOOH.$$

Instead of nitrogen trioxide, N_2O_3, we should more correctly speak of the equivalent mixture of $NO+NO_2$, but this chemically amounts to the same thing.

At the same time, I pointed out that these reactions were or might be locally modified by special circumstances in different parts of the chamber, and this matter was treated in detail in my papers of 1888.

We see at once that my theory goes back to Davy's theory of 1814, subsequently upheld, among others, by L. Gmelin and Cl. Winkler, according to which the intermediate formation of nitrososulphuric acid (chamber-crystals) is a necessary link in the chamber-process. But my new theory removes the complication of those former views, and their partial contradictions to observed facts, by denying the necessity of a reduction to NO as an indispensable factor in the process, from which reduction would follow the formation of free nitrogen peroxide in the chamber *. We will now follow up the new theory in detail and consider the modifications which the process suffers by local circumstances in certain parts of the chamber.

Let us remember that the gases of a normally working chamber contain at first an excess of NO, further on and right to the end only an equivalent mixture of $NO+NO_2$, equal to N_2O_3. *Free* nitrogen peroxide, NO_2, can be obtained only in case of irregular work, when by sending an unnecessary excess of nitrous gases into the chambers the formation of sulphuric acid has been finished too early, and the last part of the chambers contains extremely little SO_2; in this case only free NO_2 is there found. A greater or smaller excess of oxygen is without any influence on the question whether $NO+NO_2$ or more NO_2 is formed.

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* By "free" nitrogen peroxide I mean any excess of NO_2 over the proportion required to form N_2O_3 with NO, here as well as in all other places.

Although we now know that N_2O_3, when liberated from its combination with sulphuric acid, immediately dissociates for the most part into $NO + NO_2$, a very small quantity of N_2O_3 remains as such and can enter into the above-stated reaction (1) (p. 752); and according to the law of mass-action immediately more $NO + NO_2$ recombines to form N_2O_3, so that no sensible quantity of NO has time to form with oxygen "free" nitrogen peroxide, as SO_2 is present everywhere and leads to the formation of SO_5NH.

The same compound will be formed according to equation (9) (see p. 766) by SO_2 from any locally existing free NO_2.

The orange vapours filling the chambers consist of a mixture of NO and NO_2, the former being in excess in the light-coloured front part of the chamber-system, whilst later on the proportion (as shown by analysis) is almost exactly $= NO + NO_2$, which constantly again acts with H_2O, SO_2, and O to form SO_5NH, and is reformed from the latter by the action of more H_2O. We may express this either with the intermediary assumption of NOOH and N_2O_3, as in (1 *b*), (2 *b*), (3 *b*), or without this, as in (1 *c*), (2 *c*), viz.:

$$\begin{array}{lll} (1b) & SO_2 + NOOH + O & = SO_5NH, \\ (2b) & 2SO_5NH + H_2O & = 2H_2SO_4 + N_2O_3, \\ (3b) & N_2O_3 + H_2O & = 2NOOH; \end{array}$$

or else:

$$\begin{array}{lll} (1c) & 2SO_3 + NO + NO_2 + O_2 + H_2O & = 2SO_5NH, \\ (2c) & 2SO_5NH + H_2O & = 2H_2SO_4 + NO + NO_2. \end{array}$$

As before, we shall not always hamper our considerations by entering upon the complicated formulæ involved in the last-mentioned way of looking at nitrous anhydride, but we shall treat this compound as capable of existing in the state of vapour at least for a sufficient time to enter into the reactions (1); but those who prefer to do so may instead of this make use of reactions (1 *a*) or (1 *c*).

The reactions formerly assumed by Berzelius (with the qualification expressed on p. 752), R. Weber, myself, and, although but indirectly, by Raschig, namely:

$$\begin{array}{lll} (3) & SO_2 + N_2O_3 + H_2O & = H_2SO_4 + 2NO, \\ (4) & 2NO + O & = N_2O_3, \end{array}$$

cannot represent the chamber-process: for, firstly, in this case there would be everywhere in the chambers, up to the end, a large number of molecules of NO together with N_2O_3, which is not the case; and, secondly, the reaction (4) does not take place at all except in *immediate* contact with (strong) sulphuric acid; but in contact with sulphuric acid there is no free N_2O_3 formed, but SO_5NH, and we are thus forcibly brought back to reactions (1) or to reaction (7), mentioned on p. 766. If in the back parts of the chambers NO (more than required for the formula $NO+NO_2$) existed to any extent in the free state for any appreciable length of time, it would there be oxidized into nitrogen peroxide, and this in contact with either water or sulphuric acid will form nitric acid, which should be found, at least to a great extent, unchanged, as it is a sufficiently stable compound in that part of the chamber, where there is far too little SO_2 and too low a temperature to reduce much HNO_3. But since HNO_3 is *not* found in normal working back-chambers, nor in the Gay-Lussac acid, *any theory based on the reduction of nitrous vapours down to nitric oxide,* NO, *cannot be accepted as true*, as it involves the formation of "free" N_2O_4, and subsequently that of HNO_3.

It is important for our theory to notice that sulphuric acid, such as found in the chambers, certainly dissolves very sensible quantities of SO_5NH, and indeed all the "drips" and even the bottom acid of the back-chambers testify to this. But this solubility, or, as it is better expressed, the stability, of SO_5NH is greatly diminished both by a higher temperature and by dilution of the acid (comp. p. 223 *et seq.*), and this behaviour is indeed the foundation of all former processes for denitrating nitrous vitriol (p. 631 *et seq.*). In the vitriol-chambers the temperature is much above that of ordinary air; the second condition is also fulfilled, for as soon as the SO_5NH formed in one place, and floating about in the shape of a fine mist, meets with particles of water or of dilute sulphuric acid floating about as well, it must suffer decomposition according to equation (2), p. 763, so that sulphuric acid and nitrous acid are formed. Only those portions of nitrososulphuric acid which are in immediate contact with the bottom acid will be dissolved by this, and will thus be temporarily withdrawn from decomposition; but this takes place to a somewhat greater extent only in the back chambers, whilst in the front chamber, where both the higher temperature and the excess of SO_2 act as denitrating agents, the bottom acid shows little or sometimes even no "nitre."

The views hitherto brought forward do not, however, explain the whole of the vitriol-chamber process; they must be modified for the first part of the chambers, which is filled with opaque white clouds, and where Lunge and Naef have proved the existence of much NO in excess above the proportion $NO + NO_2$. The temperature is highest and the formation of acid most vivid in this region. It is not in itself impossible that here the direct reactions take place:

$$(5) \quad SO_2 + NO_2 + H_2O = H_2SO_4 + NO,$$
$$(6) \quad SO_2 + N_2O_3 + H_2O = H_2SO_4 + 2\,NO,$$

which would explain the occurrence of NO. The latter, when meeting SO_2 and O, both present here in large excess, forms directly nitrososulphuric acid:

$$(7) \quad 2\,SO_2 + 2\,NO + 3O + H_2O = 2\,SO_5NH.$$

Locally, where water is in excess, nitric acid will be formed, but here, where this acid is in the state of vapour, and where it at once meets an excess of SO_2, it is instantly reduced by the reaction:

$$(8) \quad SO_2 + HNO_3 = SO_5NH.$$

In fact in this first part of the chambers the conditions are still altogether analogous to those prevailing in the immediately preceding Glover tower, and are entirely different from those occurring in the back part of the chambers, where the temperature is lower and there is very much less SO_2 present. In the front part the NO finds such an excess of SO_2, O, and H_2O, that the formation of N_2O_4 is either altogether precluded, or if any small quantity of it is locally formed it must be instantly absorbed again, according to equation:

$$(9) \quad 2\,SO_2 + N_2O_4 + O + H_2O = 2\,SO_5NH.$$

In the first part of the chamber system free nitrogen peroxide does not and cannot exist in appreciable quantities, and therefore the formation of sulphuric acid according to equation (5) *does not play any, or no appreciable, part.* Equation (6) is practically on the same lines.

This does not yet explain why there is in fact a large excess of NO present in the first part of the chambers. We seek this explanation in a secondary reaction which under the existing conditions is bound to occur, viz.:

$$(10) \quad 2\,SO_5NH + SO_2 + 2\,H_2O = 3\,SO_4H_2 + 2\,NO.$$

This is, of course, precisely similar to that which takes place in the immediately preceding space, that is, in the Glover tower, the conditions being identical in both cases: presence of large quantities of nitrososulphuric acid, of SO_2, of H_2O, and an even higher temperature than near the top of the Glover tower, where the inflowing acid has a cooling action. Thus more NO is formed than can be at once taken up by reaction (7).

The general results arrived at are as follows:—The *principal reactions* conducive to the formation of sulphuric acid in the vitriol-chambers are, the *formation of nitrososulphuric acid* from sulphur dioxide, oxygen, and nitrous acid (eq. 1), and its subsequent *decomposition* when meeting with water or dilute sulphuric acid (eq. 2). Whether N_2O_3 exists for an appreciable time as undecomposed vapour or not, is not a decisive point in this case, as we may introduce the hydrate NOOH and as the components $NO+NO_2$ act just as N_2O_3. Besides this principal reaction, another set of reactions take place in the first part of the chambers, where the nitrososulphuric acid is partially denitrated by the excess of sulphur dioxide (eq. 10), and the nitric oxide thus formed combines directly with SO_2, O, and H_2O to reform SO_5NH (eq. 7). All the other reactions enumerated above either play no part whatever or only an insignificant part in the chamber-process, and "free" nitrogen peroxide especially does not occur at all in normally working chambers.

The mutual action of the agents meeting in the vitriol-chambers partly belongs to the class of *reversible reactions*, whose direction in one sense or another is determined by the "action of mass," one or several of the components being in excess. The direct reaction $SO_2+O+H_2O=H_2SO_4$ is *not* reversible at the maximum temperature of the lead chambers, but some of the intermediate reactions are. If oxygen or nitrous acid is in excess, the condensing reactions (1) and (7) prevail, and thus the formation of nitrososulphuric acid is induced; but if sulphur dioxide is present even only in *relative* excess, the denitrating reaction (10) prevails, and NO is split off. This does no harm in the first part of the chambers, where there is time for the NO to enter into the condensing reaction (7); but if it happens in the back part, the NO is lost, as it is not retained in the Gay-Lussac tower and escapes into the air. Another reversible reaction is that between sulphuric acid, nitrous acid, and water; where the sulphuric acid is in excess, we have:

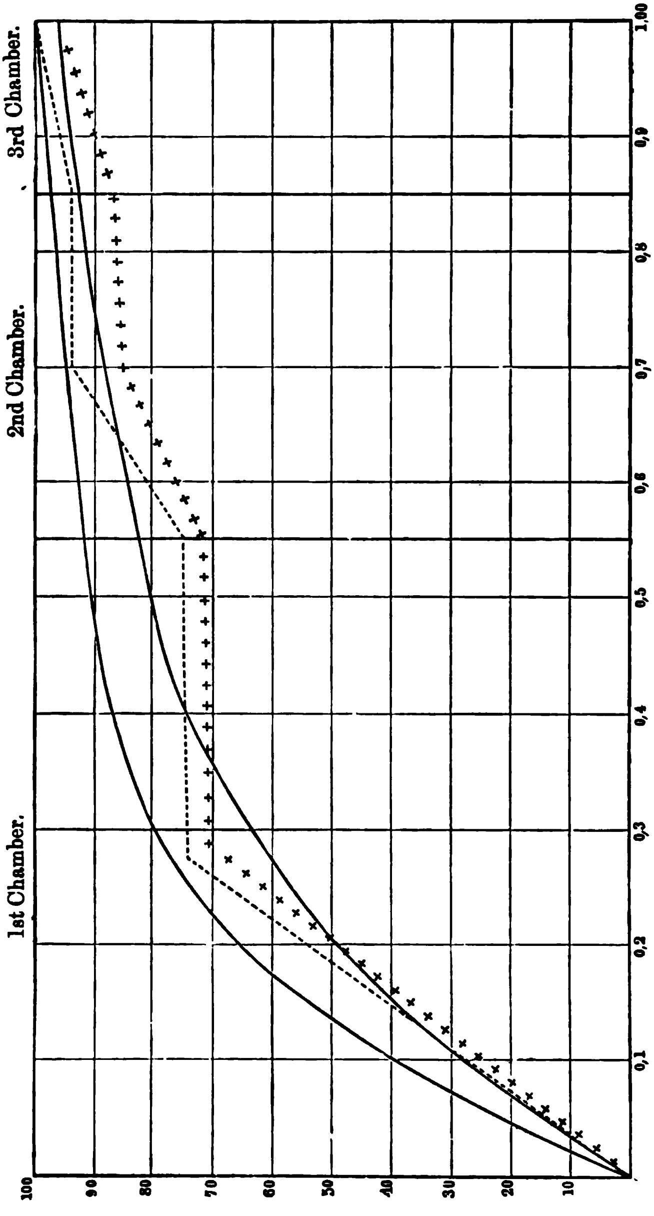
$$H_2SO_4+NOOH=SO_5NH+H_2O;$$

where, on the other hand, water is in excess, we have:

$$SO_5NH+H_2O=H_2SO_4+NOOH.$$

Nothing is more certain in the manufacture of sulphuric acid than that the process of converting sulphur dioxide into sulphuric acid takes place in a regular way only by the action of a large

Fig. 321.



excess of oxygen and of nitrous vapours; with a smaller excess of these agents sulphur dioxide escapes into the air. Both theory and practice show that even with the greatest excess of oxygen it is not possible to effect an absolutely complete oxidation of SO_2: it is generally agreed that the best practical limit is attained if the exit-gases contain 0·5 per cent. of the sulphur originally employed in the shape of SO_2. The rate at which the formation of sulphuric acid takes place under the given conditions of a certain excess of oxygen and of nitrous vapours has been mentioned before (p. 725 *et seq.*) as observed experimentally. It has also been mathematically deduced, first by Hurter (J. Soc. Chem. Ind. 1882, p. 52), afterwards by Sorel (in his frequently quoted paper); but their very hypothetical calculations lay claim to interest mostly on the ground that they are in general accordance with previously observed facts, and we must refer those interested in them to the originals*. Both authors also represent the normal working of the chambers by curves, with which Hurter compares the practical results of Mactear, and Sorel those of Lunge and Naef (which were not published at the time of Hurter's theoretical research).

We have previously (p. 731) compared Hurter's curves with the latter; in this place we will give the diagram in which Sorel represents the process (fig. 321), both by his theoretical curves (drawn in full lines)—the upper one representing a loss of 0·5, the lower a loss of 4 per cent. of sulphur—and the results obtained by Lunge and Naef (in dotted lines). I have already (p. 731) pointed out that whilst on the whole the rate of formation of the acid is in agreement with the theoretical curves, there are distinct breaks corresponding to the points where the gases leave one chamber to enter the next, and we have to some extent gone into the explanation of this phenomenon. But it is now time to give Sorel's explanation, which, although in full agreement with my theory of the vitriol-chamber process, amplifies it by specifying more distinctly the conditions under which either the first or the second of the main reactions,

$$(1)\quad SO_2 + NOOH + O = SO_5NH,$$

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* Sorel (Fabr. de l'Ac. sulf. p. 566) maintains that the first proposition of Hurter's is self-evident, but that the remaining propositions are mathematically untenable; moreover, that some of Hurter's conclusions, drawn from his mathematical reasoning, are partly contrary to experience. So much is certain, that practice has not profited in any respect whatever from his theory.

$$(2)\quad SO_5NH + H_2O = H_2SO_4 + NOOH.$$

takes place.

In an inert atmosphere nitrososulphuric acid will give up more or less N_2O_3, according to the concentration of the sulphuric acid, the quantity of nitrous (or nitrososulphuric) acid, and the temperature. If a certain quantity of N_2O_3 is removed from the surrounding gases, either directly or by reduction to NO, the acid will yield up more N_2O_3; if, on the other hand, the surrounding atmosphere becomes richer in N_2O_3 by oxidation of NO, the acid will again take up some N_2O_3. The tension of N_2O_3 in its solution in H_2SO_4 is increased by a rise of temperature, but much more by diluting the acid. If, therefore, there exist in an atmosphere, containing a certain quantity of N_2O_3, two solutions of N_2O_3 in sulphuric acid, one of them in concentrated, the other in dilute sulphuric acid, the former will enrich itself in N_2O_3 at the expense of the latter, even if it be to a certain extent hotter than the latter. Even the presence of SO_2 does not prevent the solution of N_2O_3 in sufficiently concentrated acid, provided that oxygen is present in excess and that the tension of the N_2O_3 (actually present or possible to be formed from NO and O) is greater than that of the acid in question. On the other hand, the SO_2 will decompose (*i. e.* denitrate) the acid if the outer tension of N_2O_3 is less than that of the acid, or on diluting the latter, or on raising the temperature. [These are indisputable facts, well known before Sorel, but very clearly put by him with the addition of bringing in the "tension" of N_2O_3, about which he could not have known very much in detail, and which, in the light of modern theories, we should partly or entirely replace by the mass-action of the vapours. Much more material for deciding these questions has been furnished by my own and my assistants' investigations, p. 227 *et seq.*]

We will, for instance, assume a certain definite quantity of acid of 57° B. (= 130°·4 Tw.), containing so much N_2O_3 that for a specified temperature the equilibrium with the surrounding gaseous mixture is established. This acid hovers as a mist in the gaseous mass. Suppose a certain volume of this gaseous mass is cooled down, the pressure remaining the same; then part of the aqueous vapour contained in the gaseous mixture will be precipitated in a liquid form and will dilute the acid. The acid will thus become incapable of withdrawing all its N_2O_3 from the influence of the

SO_2 present; some NO will be formed, but also some H_2SO_4, by which the acid becomes more concentrated. If now the gaseous mass is brought back to the former, higher, temperature, the acid must, in accordance with the rise of temperature, yield up aqueous vapour, till it has again attained the density = 57° B., at which it once more fixes NO and O in the shape of N_2O_3.

Leaving out of consideration the secondary reactions, Sorel, like myself, regards the intermediate formation of nitroso-sulphuric acid (the fixation of oxygen upon sulphur dioxide by means of nitrous acid) as one of the principal reactions, followed by the decomposition of that compound, by dilution with water, into sulphuric acid and nitrous acid.

The principal cause for determining the reaction in this or that sense is a *change of temperature.* We have seen before (p. 715) that the temperature near the leaden walls of the chamber is considerably less than that of the inner parts; therefore the gases must assume a quick rotation round a nearly horizontal axis, and each minute drop of acid, according to the change of vapour-tensions, must first be concentrated in the central portion and then be diluted again near the walls. Suppose we have a chamber-acid of 116° Tw. or 67 per cent. H_2SO_4. If, as was the case in a special experiment, the temperature next to the walls is = 75°, that in centre = 90°, the vapour-tension of 67 per cent. acid next to the wall will be = 27 millim. (comp. the table p. 196); and since the acid hovering in the centre must have the same vapour-tension, but the higher temperature of 90°, its concentration (according to the same table) must be = 73 per cent. H_2SO_4 or = 130°·4 Tw. If, for instance, the acid near the wall had contained only 64 per cent. H_2SO_4, its vapour-tension would have been = 37·4 millim., and the hotter acid in the centre would at equal tension have contained 71 per cent. = 126° Tw. A number of observations made by Sorel at working-chambers show that the above-supposed differences do exist, which proves that the assumption of an equal vapour-tension all over the chamber is correct, and consequently also the assumption that regularly the concentration of the acid is greater near the centre than near the walls, where the cooling action of the air is at play. But as the greater concentration of the acid favours the fixation of nitrous vapours by SO_2 and O, in the shape of SO_5NH, and the greater dilution the decomposition of this compound into H_2SO_4 and N_2O_3, it follows that the formation of SO_5NH takes place chiefly in the centre, and that of real H_2SO_4 principally near the walls. The neighbourhood of the walls thus increases the production, as the cooling brings about the condensation of water, the dilution of the nitrous acid, and its decomposition into H_2SO_4 and N_2O_3. To a smaller extent this is also effected by the neighbourhood of the acid layer at the bottom, which is both cooler and more dilute than the acid floating about in the centre. All this is indirectly, but certainly, proved by the fact that a few centimetres from the wall, where the formation of H_2SO_4 must be strongest, and equally a little above the bottom acid, the greater intensity of the reactions is manifested by a rise of temperature.

As the gaseous current moves nearer the end of the chamber it becomes poorer in SO_2, and the reactions are therfore less intense. Moreover, observation shows that the temperature in the second half of the chamber hardly sinks at all in the centre, and but 2° near the walls. Less H_2SO_4 being made in this part, the acid in the centre is more dilute, and less able to fix N_2O_3 and SO_2 in the shape of SO_5NH, and that at a time when the smaller quantity of SO_2 anyhow makes this reaction more difficult. This, according to Sorel, explains the almost total cessation of the reactions in the back part of the first chamber, observed by Lunge and Naef; and it also explains the revival of the process in the second chamber, observed by them, as the gases are *cooled* near the end walls of the chambers and in the connecting-pipe to the extent of 20° or 30° C. In fact a chamber exposed on the north side to the free air, and on the south side to the radiation from a second chamber, made at the north wall $2\frac{1}{2}$ times more acid 3° Tw. stronger than at the south wall.

There must be a close connection between the temperature at the chamber-wall, the nitrous-acid tension, the intensity of the reactions at any given point, and the outside temperature. For every description of chambers, every special place in them, and every rate of manufacture, a certain temperature must be the most favourable—that which causes neither too much nor too little vapour-tension under the given circumstances. Both when the temperature is too high or when it is too low more nitre is used than under normal conditions [the damage done by too low a temperature is doubtful; compare the Freiberg experiences, p. 712].

In the case of the high-pressure style of working, where the temperature is higher to begin with, any rise of the outside temperature makes less difference. Many French manufacturers have adopted this high-pressure style (brought about by a very large supply of nitre, by means of ample Gay-Lussac and Glover space, comp. pp. 468, 497, 561, 624, &c.), where the draught is better and the cost of plant less; but this can only be done with medium-sized chambers, as otherwise the heat rises too much at the commencement.

We see how important, in Sorel's view, is the part played by the division of the total chamber-space into several chambers. We cannot doubt that in reality the cooling-action of the chamber-walls and ends and of the connecting-pipes is very important. But Sorel does *not* explain why, according to his own showing, the chamber temperature sinks very little in the second half, and very little acid is made there, although the surface of lead on this part of the two long sides and the roof is very much larger than on the two ends and the connecting-pipes taken together.

This seems to prove that the cooling is nothing like the *all-*important factor assumed by Sorel, and that the more intimate mixture of gaseous and liquid particles in the connecting-pipes and the shock against the solid surfaces which brings about a condensation of the particles of mist to larger drops, where the *liquid* substances meet and react upon each other, must be equally acknowledged as potent factors for explaining the anomaly exhibited in the curves, figs. 309 & 310, p. 730. In my own proposals for modifying the chamber system, as explained on p. 478 *et seq.*, all the influences for reviving the chamber-process are brought into action,—that of an intimate mixture, of the shock against solid surfaces, and of the dilution of the acid by water, which at the same time serves as a cooling agent; and we have also seen (p. 497 *et seq.*) that many years' practice has now proved the efficiency of those proposals to which I had been led, firstly by the experiments made by myself with Naef on the Uetikon chambers, secondly by my theoretical views as they were gradually evolved from both factory and laboratory work.

Ostwald (at the Congress of Electrochemists in 1895 and the German Naturforscher-Versammlung in 1901; 'Grundriss der Allgemeinen Chemie,' 3rd edition, p. 516) has pointed out that the nitrous vapours in the lead-chamber process act merely as catalyzing agents, by greatly increasing the speed of the otherwise very slow and incomplete reaction: $SO_2+O+H_2O=H_2SO_4$. Of course no objection can be made against extending the class of "catalytic processes," with which we must of necessity deal when speaking of the manufacture of sulphur trioxide in Chapter XI., so as to embrace the vitriol-chamber process as well *. But, as I have shown in Zsch. angew. Ch. 1902, p. 148 *et seq.*, it would be a grave error if we imagined that we are *explaining* that (or any other) process by calling it "catalytic," or that by giving it that name we may detract from the minute investigation of the *intermediary reactions.* On the contrary, only the latter can lead up to a real "explanation" of the process, just as will be shown in Chapter XI. In the present case Ostwald's enunciation has caused some little mischief, as others (like Th. Meyer), on the alleged authority of that eminent theoretical chemist, believed they might neglect as unessential the intermediate reactions between the nitrogen oxides and the other substances present. Ostwald himself did *not* go so far, he simply said that the assumption of intermediate products is not suitable for all cases; but proof should be given that the intermediate reactions in fact proceed more quickly than the direct reaction. *But in the present case this proof is abundantly afforded by the experience of many generations, and is constantly repeated by every teacher of chemistry.* While the formation of sulphuric acid by the direct action of SO_2 on air and water is notoriously an extremely slow and incomplete process (p. 750), every lecturer on chemistry shows the *instantaneous* formation of chamber crystals when the above reagents meet with nitrous vapours, and the equally *instantaneous* decomposition of these crystals when meeting an excess of water. I cannot conceive a more complete fulfilment of the condition demanded by Ostwald, and a more utter *deductio ad absurdum* of those who would henceforth consider the reactions of the nitrous vapours in the lead chambers as unimportant "by-reactions" whose study is not essential for arriving at a theory of the chamber-process.

Several papers on the theory of the vitriol-chamber process, published within the last few years, can be only briefly quoted, as they contain nothing of importance.

Loew (Zsch. angew. Chem. 1900, p. 338) tries to apply the law of the action of masses to the above process. But, as I have shown (*op. cit.* 1902, p. 146), he makes inadmissible simplifications and other erroneous assumptions which render his reasoning futile.

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* We shall see later on that this process must not be classed among "pure catalytic processes," but among "pseudo-catalytic" ones.

Th. Meyer (*op. cit.* 1901, p. 1245) even makes a much less successful attempt in the same direction. I have shown (*op. cit.* 1902, p. 147) that he has entirely misunderstood the law of the action of masses and has, moreover, committed so many other grave mistakes that there is no occasion to discuss his paper here, the less so as he has entirely acknowledged the justice of my remarks (*op. cit.* 1902, p. 278).

The discussion as to the possibility of establishing a mathematical theory on the above lines has been continued, without any practical result, by Riedel (*op. cit.* 1902, p. 462), Lunge (*ibid.* p. 581), Haagn (*ibid.* p. 583), Riedel (*ibid.* p. 858), Lunge (*ibid.* p. 931), Keppeler (*ibid.* p. 809).

Of much greater importance is the paper, which we shall now refer to, viz. Brode's, in Zsch. f. angew. Chem. 1902, p. 1081. He broadly surveys the laws of chemical dynamics, and I shall give a short abstract of this paper, so far as it concerns our subject. Theoretically every reaction may be regarded as incomplete at any temperature, since our analytical methods will never be sufficiently exact to detect the minutest traces of unchanged substances. But practically we must regard those reactions as *complete* in which the products of one side of the equation cannot be altogether *detected* and in which the reaction proceeds entirely in the ratio of the equivalent weights. These reactions are denoted by the mark of equality =. *Incomplete* are those reactions which are *reversible*, and which are denoted by the mark $\rightleftarrows$ (van't Hoff). At ordinary temperatures, for instance, the reaction $2H_2+O_2=2H_2O$ is complete, at high temperatures it is incomplete:

$$2H_2+O_2\rightleftarrows 2H_2O.$$

Nearly all reactions are incomplete at high temperatures, and at extreme temperatures the reaction would be complete in the sense:

$$2H_2O=2H_2+O_2.$$

If we enquire how far different reactions actually take place, that is, if we regard the position of equilibrium, we find enormous variations which we ascribe to the difference of chemical affinities. We measure these by the "constant of equilibrium," which, according to the law of the action of masses, has the following meaning :—For every reaction at constant temperatures the product of the concentrations of the reacting substances on one side of the equation, divided by the product of the concentrations of the substances on the other side, possesses a constant value, if we state the cencentration in "moles" (gram-molecules per litre). If two, three, or *n* molecules react at the same time, in lieu of the simple concentrations the second, third, or *n*th power must be assumed. The constants are therefore independent of the concentration and remain unchanged for every reaction at certain temperatures. In the case of incomplete reactions their order of magnitude does not differ very much from unity; in the case of complete reactions their value approaches zero. The law of the action of masses admits of computing the shifting of concentrations consequent upon adding an excess of one of the components to a mixture in the state of equilibrium. If, for instance, in the reaction $c_1 + c_2 \rightleftarrows c$ the three substances are at equilibrium, they are in the relation: $\frac{c_1\,c_2}{c^2} = \text{const.}$ If we now add to c_2 another quantity $= a$, there will be a change of x molecules in the sense of using up somewhat more of the substance c_2; when the equilibrium is again reached, the concentration of the second component will not be $c_2 + a$, but $c_2 + a - x$, and the concentrations will fulfil the following conditions:

$$\frac{c_1\,c_2}{c^2} = \text{const.} = \frac{(c_1 - x)(c_2 + a - x)}{(c + x)^2}.$$

This admits of computing the value of x. If one of the components is in great excess, the concentration of the other component can be reduced to a very small value.

Van't Hoff has shown how the reaction-constants can be quantitatively computed from the "heat-toning" of the reaction. From this follows further that on the shifting of the equilibrium a phenomenon sets in which opposes the shifting and partially undoes its effect; hence any shifting through an elevation of temperature will be combined with a reaction which *absorbs* heat, and *vice versa*; at extreme temperatures only such reactions will occur which absorb heat (formation of CS_2, CaC_2, NC—CN). By increasing the *pressure* those reactions are promoted which reduce the total number of molecules.

But the laws of chemical equilibrium enlighten us only upon the *final state* into which a reacting mixture enters and whereupon no further spontaneous change takes place; they do not state anything concerning the *velocity of reaction,* the factor of time not finding any place in thermodynamical equations. Concerning this subject we may establish the following specifications:—

1. With increasing concentration of the substances *vanishing* during the reaction, the reaction velocity g increases, and in *complete* reactions is proportional to the concentrations of the moles per litre; thus: $g = kc_1c_2$; k being a constant to be found by experiment for each reaction and each temperature. On the other hand, the concentration of the *newly formed* substances comes into play only in *incomplete* reactions. Here g is the difference of two opposite reactions; the newly formed substances, c_1, c_2, causing a change in one direction, the vanishing substances c_3, c_4, a change in the opposite direction: $g = k_1c_1c_2 - k_2c_3c_4$.

In the state of equilibrium $k_1c_1c_2 = k_2c_3c_4$, hence $g = 0$. The equilibrium-constant k is the quotient of the two opposite velocity constants $\frac{k_1}{k_2}$. When a substance does not react with one molecule, but with n molecules, properly speaking the concentration ought to be expressed in the nth power in the equation of velocity, but experiment has generally shown that lower powers must be assumed. If the reaction goes on step by step, only one of which requires sensible time, the others proceeding with extreme velocities, the total reaction must proceed with the velocity of the slow intermediate reaction.

2. The influence of *temperature* is always felt by an enormous *increase of velocity on raising the temperature.* Generally raising the temperature $n \times 10^\circ$ increases the velocity by $2{\cdot}5n$; for instance $30^\circ = 2{\cdot}5 \times 2{\cdot}5 \times 2{\cdot}5$. Thus a process which at 100° requires an hour, at 0° will take a year.

3. By means of *catalyzers* the velocity may be increased to such an extent that a reaction which by itself has an infinitely small velocity ($= 0$), after adding a certain substance, which remains unchanged during the reaction, is effected in an immeasurably short time. As *pure catalysis* we denote the cases where intermediate reactions are impossible or unlikely; as *pseudo-catalysis* (Wagner) those cases in which intermediate reactions are proved or probable. Neither kind of catalyzers can shift the position of

equilibrium; otherwise we should attain to a *perpetuum mobile*. Catalyzers cannot possibly influence the free energy of a system; they merely influence the time of reaction. What causes the difference in velocity of various reactions is an entirely unsolved problem.

The application of the above to the theory of the formation of SO_3 from SO_2 and O will be referred to in the 11th Chapter. Here we consider merely how far we can apply the hitherto attained results of chemical dynamics to the lead-chamber process. Brode agrees with me in holding that in this process, where hydrated sulphuric acid is *practically completely* formed at a maximum temperature of 90°, the laws of chemical equilibrium cannot be applied. We can only think of applying the laws of the velocity of reactions. Elsewhere we always notice an increase of velocity with increasing temperatures; how, then, can a complete reaction have an *optimum* of temperature? The explanation is this: that the pseudo-catalytical action of the nitrogen oxides in the chamber is founded on two intermediate reactions of different velocity. In such cases the time required by the entire reaction always depends upon the slower of the intermediate reactions. Since in the lead chamber water is always present in the shape of mist, the process goes on in two phases, the liquid and the gaseous. With an increase of temperature more and more aqueous mist is changed into steam. But nitrososulphuric acid requires *liquid* water for its decomposition, so that with the decreasing concentration of the latter the velocity of one of the intermediate reactions must equally decrease. Moreover this reaction is incomplete with low concentrations of water. We have thus an interesting case of pseudo-catalysis. The direct reaction is practically not reversible, nor is the first of the intermediate reactions*, but the second of these (the decomposition of nitrososulphuric acid by water) is reversible. Consequently after some time nothing remains of the original SO_2, but part of the SO_5NH will remain undecomposed, since for practical reasons, sufficiently elucidated in the text of this chapter, it is not feasible to employ in the last chamber a sufficient excess of water to completely decompose the nitrososulphuric acid. Thus a considerable quantity of the latter must remain up to the last, and it would be removed with the inert nitrogen and oxygen if it were not retained by the Gay-Lussac tower. This theory has explained the reason of the fact, known to practical acid-makers for more than half a century, that there must be a large excess of nitrogen oxides in the last chamber if the conversion of SO_2 into H_2SO_4 is to be practically complete.

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* Comp. (p. 224) my observations as to the great stability of nitrososulphuric acid in the absence of water.

Since in the lead chamber, as in every heterogeneous process, the velocities of condensation and absorption also essentially influence the total velocity, the phenomena are very complicated and are not yet accessible to mathematical treatment; hence a dynamical theory of the formation of sulphuric acid in the lead chamber cannot yet be established.

In his excellent treatise 'Die Elemente der chemischen Kinetik' (Wiesbaden, 1902), Bredig equally shows that the quantitative working out of the intermediate reactions in the lead-chamber process must be an extremely complicated problem of chemical kinetics, which is not likely to be realized very soon. Until it is known we must be content with my above-given demonstration, that there is an enormous difference in velocity between the direct oxidation of SO_2 by O and the intermediate reactions postulated by me, which cannot be reactions of secondary importance, since they always occur *immediately* and *quantitatively* whenever the components meet.

CHAPTER VIII.

THE PURIFICATION OF SULPHURIC ACID.

COMMERCIAL sulphuric acid, as it is produced in the chambers, always contains a number of impurities, partly owing to the raw material, especially the pyrites, partly to the nitre, the water, the lead of the chambers, &c. Since this acid, if at all, is usually purified at the stage at which we have now arrived, viz. as chamber-acid, before being concentrated, we shall now treat of this subject, although, in the great majority of works, the chamber-acid is never purified, nor is there any occasion for it. For the sake of completeness, we shall here describe also the manufacture of pure distilled oil of vitriol, although this already presupposes the concentration of acid on a large scale, to be subsequently described.

The impurities of chamber-acid may consist of:—arsenic acid, arsenious acid, antimonic oxide, selenium, thallium, lead, zinc, iron, copper, mercury, calcium, aluminium, alkalies; further, sulphurous acid, nitric acid, nitrous acid, nitric oxide (in the presence of ferrous sulphate), organic substances. According to Kuhlemann, for instance (Wagner's Jahresb. 1872, p. 253), the acid of two Harz works contained to each 100 grams SO_3:—

	a.	*b.*
Arsenic.........	0·0088 grm.	0·0174 grm.
Antimony......	0·0394 ,,	trace.
Copper.........	0·0013 ,,	,,
Iron............	0·0081 ,,	not estimated.
Zinc............	0·0087 ,,	,,
Lead............	trace	0·0231 grm.

Selenium occurs very frequently in sulphuric acid, where its presence is more and more noticed (*e.g.* Davis, J. Soc. Ch. Ind.

1883, p. 157, and Lunge, Ch. Ind. 1883, p. 128); its occurrence in the flue-dust and the chamber-deposit is well known.

Most of these substances occur partly in too small a quantity in the acid to be injurious, and they are partly without any influence for most uses of sulphuric acid; the lead, for instance, is almost entirely precipitated on diluting the acid, the iron during its concentration in the platinum still, in the shape of pink crystals of anhydrous ferric sulphate. But there are cases where these impurities may cause trouble. Thus, according to Deutecom (Chem. Zeit. 1892, p. 574), a minute quantity of *mercury* makes sulphuric acid less suitable for pickling brass objects. *Nitric acid* causes wool to be stained yellow in the "carbonizing" process. *Platinum* renders the acid unsuitable for electrical storage-batteries. *Iron* sometimes causes a pink colour, which is removed by a little nitric acid, sometimes even by the action of atmospheric air. [This looks as if the pink colour was not caused by iron, but by selenium.] Sorel ('Fabrication,' p. 414) states that *selenium* is prejudicial to the acid required for parting gold and silver. Drinkwater ('Analyst,' viii. p. 63) holds the same view with respect to the purification of mineral oils.

These are, however, exceptional cases.

The only two impurities which cause much trouble for many applications of sulphuric acid are *arsenic* and *nitrogen acids*—the former from a sanitary point of view*, the latter owing to the action of the nitrogen acids on the platinum stills; and most methods of purification therefore aim at the removal of these substances.

Methods of Purification.

Apart from the cases where impurities are at least partially removed from sulphuric acid in the manufacturing process itself, *e. g.* the constituents of flue-dust by the Glover tower, the iron, the crusts forming in the platinum stills, &c., special purifying processes are sometimes employed either because some impurity (*e. g.* arsenic) occurs in an unusually large quantity, or else very pure acid is required for special purposes. Different methods must be employed for different cases, but the most important of these refer to the removal of arsenic and to that of the nitrogen compounds. If acid is treated for the removal of arsenic by H_2S, nearly all the other inpurities are removed at the same time.

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* We need only point to the "beer-scare" of 1900, consequent upon the mischief done by drinking beer brewed with addition of glucose which had been prepared by means of sulphuric acid with an extraordinarily high percentage of arsenic, some of which remained in the glucose.

Frequently sulphuric acid is *muddy*. A very slight quantity of lead sulphate and especially of selenium may cause this, nor is the muddiness always removed by dust-chambers. This is more easily effected, up to a residue of about 3 milligrams per litre, by making the acid slowly traverse several chambers, if possible in a zigzag direction. At Griesheim the acid is practically clarified by means of a small tower filled with pebbles, but not fed with any liquid, and interposed between the burners and the Glovers; the dirty acid condensing here shows about 85° Tw. Coarser solid matters may be removed by sand-filters, but these frequently do not effect a clarification of sulphuric acid from selenium or other very finely divided substances. This is such a frequent case that many buyers do not object to the turbid appearance of the acid, which in reality does not interfere with its use in the great majority of cases. Good filters for turbid sulphuric acid, capable of making it thoroughly limpid in every case, are not yet known.

The Purification of Sulphuric Acid from Arsenic.

Arsenic is found rarely, and never in more than insignificant traces, in acid which has been made from brimstone: most of the latter material, by far, is used where acid free from arsenic is wanted. On the other hand, most kinds of pyrites contain arsenic; and the acid obtained from pyrites is therefore arsenical, but in very different degrees, according to the percentage of arsenic in the pyrites and to the mode of manufacture.

The percentage of arsenic in pyrites is stated very differently: whilst most analyses of the ordinary ores only show "traces" up to fractions of 1 per cent., H. A. Smith asserts that he has found much larger quantities in the ores most commonly employed, viz. in Westphalian pyrites 1·878, in Belgian pyrites 0·943, in Spanish 1·651, in Portuguese 1·745, in Norwegian 1·649–1·708 per cent. of arsenious acid. These analyses are decidedly suspicious since their results differ so much from all others. Nor can we accept his estimations of arsenic in the various products of the alkali manufacture, derived from the original arsenic in the pyrites, his results being extraordinarily high (details in our first edition, p. 462).

Stahl (Zsch. f. angew. Chem. 1893, p. 54), in working Spanish pyrites, found in the acid of the first chamber 0·16 per cent. As_2O_3, in the second 0·01 per cent., in the third 0·007 per cent., and in the last chamber only a trace. When working purer pyrites from Virginia or New England, the acid of the first chamber contained 0·005 per cent. As_2O_3, the second nothing, the average 0·002 per cent., all calculated on acid of 66° Bé.

Bräuning (Preuss. Zsch. f. Berg- etc. Wesen, 1877, p. 142) states that the chamber-acid made at Oker contains on an average 0·05 per cent. arsenic (and 0·008 per cent. antimony). At Freiberg, in 1880, according to direct information, the chamber-acid contained generally 0·02 per cent., but sometimes up to 0·14 per cent. arsenic. Later on we shall see how it stood there in 1902.

Hjelt (Dingl. Journ. ccxxvi. p. 174) found in Westphalian pyrites only 0·30, in Norwegian only traces, in Spanish pyrites on an average 0·91 per cent. of As. Of the latter there remained in the cinders 0·19 per cent., in the saltcake none; in the hydrochloric acid: (*a*) pan acid of 38° Tw., 0·066 per cent.; (*b*) drier acid of 32° Tw., 0·014 per cent. This proves that the $AsCl_3$ mostly volatilizes in the pan. So far as the sulphuric acid is concerned, Hjelt found, with the same Spanish pyrites, containing 0·91 per cent. of As, for each 100 parts of H_2SO_4, in the

Chamber acid	0·202 As,	of which	0·040	as As_2O_5.
Glover-tower acid	0·331 „	„	0·041	„
Gay-Lussac-tower acid ...	0·341 „	„	0·132	„
Acid of the last chamber .	0·019			

The higher proportion of the Glover-tower acid comes from the arsenic contained in the gas; the increase of arsenic acid in the Gay-Lussac tower is, of course, caused by the oxidizing action of the nitrous vitriol.

I am informed by Mr. G. E. Davis that, in 1902, his acid from Rio Tinto pyrites, as it went to the saltcake department 135° Tw. strong, contained on an average 4·83 grams As per litre.

Hehner (J. Soc. Chem. Ind. 1901, p. 188) takes the average of As_2O_3 in ordinary, unpurified pyrites acid = 0·2 per cent. "Purified" acid ought not to contain more than 1 part As_2O_3 in 200,000 of acid, according to the same authority.

According to G. E. Davis (Chem. News, xxxvii. p. 155), in the Glover tower all arsenic acid is reduced to arsenious acid by the burner-gas, and in the Gay-Lussac tower all is again converted into arsenic acid. This assertion is not in accordance with the analyses of Hjelt just quoted, nor with my own analyses, in which I always found both degrees of oxidation of arsenic at the same time.

Filhol and Lacassin found in three samples of "pure" commercial sulphuric acid, per kilog.:—1·2870 grm.; 0·5691 grm.; traces of As_2O_3 (Wagner's Jahresb. 1862, p. 212). Further estimations of arsenic in commercial sulphuric acid, according to Schnedermann, Kerl, Filhol, &c., will be mentioned later on; those of Kuhlemann have already been given, p. 780.

Of course, even with the same raw material, the arsenic in the sulphuric acid will vary, according to whether the gas-pipe leading from the burners to the chambers offers more or less opportunity for depositing arsenical flue-dust. When employing a Glover tower the chamber-acid contains rather less arsenic, because a large portion of it is deposited at the bottom of the tower in the shape of mud, but the acid from the tower itself may occasionally contain all the more arsenic.

At the Freiberg smelting-works, where mixed ores containing from 2 to 2·5 per cent. of As are employed, about 97 per cent. of the arsenic is condensed in the large and well-cooled dust-chambers, described p. 393, so that the acid contains mostly only 0·02 per cent. of As, only exceptionally up to 0·14 per cent., whilst formerly it amounted to 0·25 or even 0·5 per cent. (comp. p. 394).

The acid made from the very pure pyrites found in some localities in the United States (p. 57) is, of course, free from arsenic.

On the detection and estimation of arsenic in sulphuric acid, comp. *supra* pp. 248 and 252, and *infra* the Appendix concerning the publications issued during the printing of this volume.

In most cases where sulphuric acid is employed a small percentage of arsenic is of no consequence—for instance, in superphosphate, or in sulphate of soda to be used for alkali- or glass-making. Probably sulphuric acid, when employed for these operations, is never subjected to a purifying process. In the latter case certainly most of the arsenic passes over into the hydrochloric acid and can be traced there. When the hydrochloric acid is used for generating chlorine, the arsenic does no harm; for although it probably passes over, at any rate partly, into the chloride of lime, it will only occur in this as the insoluble and innocuous calcium arseniate. Much more harm is caused by arsenic in the sulphuric or hydrochloric acid which is employed in the food-industries, for instance in the manufacture of starch-sugar, of tartaric acid, in the fermentation of molasses, for pressed yeast, for washing the regenerated char of sugar-works, &c. A. W. Hofmann has reported a poisoning-case in which bread was contaminated with arsenic by the use of arsenical hydrochloric acid along with soda to make the dough rise. It is unnecessary to speak of medicinal uses, since for them crude sulphuric or hydrochloric acid is never supposed to be employed.

But even for some purely technical uses arsenic in sulphuric (or hydrochloric) acid is not allowable :—on the one hand, for the preparation of certain colours, for tinning iron (sheet-iron cleaned with arsenical sulphuric acid is here and there covered with spots of reduced arsenic, which will not take the tin coating—see Gossage in Hofmann's Report by the Juries, 1862, p. 12); on the other hand, for the manufacture of preparations which serve for food or medicine, and into which a portion of the arsenic might pass over. To these belong tartaric, citric, phosphoric acids, glucose, milk of sulphur, sulphide of antimony, &c. Even in Doebereiner's lighting-machines arsenical acid must be avoided, since the arseniuretted hydrogen evolved in them would soon spoil the platinum sponge. It has also been observed that ammonium sulphate made from ammoniacal gas-liquor by means of strongly arsenical sulphuric acid turns yellow, no doubt in consequence of the formation of sulphide of arsenic. It is mentioned in our third volume, in describing Deacon's chlorine process, that arsenical sulphuric acid here seems to do great harm also.

In some cases, therefore, it is of importance for the producers of strongly arsenical acid to make it more saleable; and a number of methods of purification have been proposed with this object. None of them seems to produce an acid absolutely free from arsenic, but sufficiently so for all practical purposes. Bloxam (Pharm. Journal, [2] iii. p. 606), by employing his electrolytical method for the discovery of arsenic, found that all samples sold as "chemically pure" contained traces of it, and that acid absolutely free from arsenic cannot be obtained in any other way than from pure sulphur dioxide and nitric oxide in glass apparatus at a low temperature, avoiding all cork or india-rubber; the gases themselves must be evolved cold or at a very moderate heat.

The following methods have been employed for the separation of arsenic from sulphuric acid:—

(1) *Distillation* of the sulphuric acid (Bussy and Buignet, Dingl. Journ. clxii. p. 454) is said to effect this purpose, even more completely than precipitation by sulphuretted hydrogen, provided that the arsenic is all present as *arsenic acid*, which remains entirely behind in the residue; if, however, arsenious acid be present, it is carried over with the sulphuric acid. Since the sulphuric acid of commerce mostly contains arsenious acid, it should be treated with nitric acid, in order to convert all the arsenic into arsenic acid; then the acid must be mixed with a little ammonium sulphate (in order to destroy the nitrous acid) and distilled. In this case the arsenic is said to be removed more completely than by sulphuretted hydrogen or barium sulphide; at the same time the dilution of the acid, necessary in the latter case, is avoided. But the distillation of sulphuric acid is an operation somewhat difficult on the large scale, and is not applicable for the purification of chamber-acid.

According to Blondlot (Compt. Rend. lviii. p. 76), the employment of ammonium sulphate is objectionable, because by an excess of it arsenic acid is again reduced. He therefore recommends heating the acid with peroxide of manganese or potassium permanganate. Bussy and Buignet deny that an excess of ammonium sulphate reduces arsenic acid (Compt. Rend. lviii. p. 981). Maxwell Lyte (Chem. News, ix. p. 172) says the statement of Bussy and Buignet, that arsenic does not distil over unless present as arsenious acid, is correct; but in order to obtain from the first a product completely free from nitrogen compounds, he destroys the latter by adding to the sulphuric acid $\frac{1}{4}$ to $\frac{1}{2}$ per cent. of oxalic acid, heating in a porcelain dish to 110° C. with continuous stirring, cooling down to 100° C., and adding potassium bichromate in the state of powder or as a solution in sulphuric acid, till the green colour has been changed to greenish yellow and the presence of free chromic acid is thus indicated. All the arsenic is now converted into arsenic acid; and on distillation a perfectly pure acid is at once obtained. Permanganate of potash performs the same service, but is more expensive.

The process of Menzies, which will be described in the next Chapter, is asserted to be at the same time a process for removing the arsenic in the shape of arseniate of iron, but it does so only very imperfectly, as we shall see.

(2) *Removal of the arsenic as trichloride.*—The trichloride boils at 125° C.; it is therefore completely volatilized on heating, long before the sulphuric acid has begun to boil: this process can be used without diluting the latter. With this object Otto and Löwe proposed heating the acid with common salt (Dingler's Journal, cxxxii. p. 205); Graeger, heating with barium chloride, because the action in this case in not so rapid (ib. clv. p. 236); Buchner (in 1845) recommended conducting a current of hydrochloric-acid gas into boiling sulphuric acid and expelling the hydrochloric acid by heating in the open air. Bussy and Buignet have proved that in this way acid free from arsenic cannot be obtained; but Buchner (Chem. Centralbl. 1864, p. 600) asserts that this is due to the presence of arsenic acid, and that an acid entirely free from arsenic is obtained by first reducing the arsenic acid contained in the sulphuric acid by heating it with charcoal, when the sulphur dioxide evolved causes the reduction; this can also be done when introducing the current of hydrochloric-acid gas. If Buchner's statement is correct, the troublesome operation of distilling the acid is unnecessary. Schwarz (Wagner's Jahresb. 1865, p. 232) heats the acid for some time with 1 per cent. of common salt and ¼ per cent. of charcoal dust under a chimney with a good draught—which comes to the same thing, and appears to be more convenient; but on carrying it out on a large scale great difficulties arise from the fact that the process does not work with dilute acid, and that after the introduction of common salt into concentrated acid the glass retorts often crack. According to Tod (Liebig's Jahresb. 1856, p. 292), if a current of HCl is introduced, heating to 130°–140° is sufficient, while if common salt be employed the acid must be heated to 180°–190° C., in order to expel the arsenic trichloride.

Selmi (Berl. Ber. 1880, p. 206) dilutes the acid with half its volume of water, adds some lead chloride, and distils off the first portion, in which all As is contained as $AsCl_3$. Hager (Chem. Zeit. Rep. 1888, p. 234) repeats the same proposal, adding that the employment of chloroform, proposed as useful in this operation, may lead to dangerous explosions. The acid, after being decanted from the lead sulphate, is to be submitted to fractional distillation.

(3) *Precipitation of the arsenic as sulphide.*—This is the only operation carried out on a manufacturing scale, and it offers the additional advantage that, apart from the arsenic, several other impurities are precipitated (such as lead, antimony, selenium) and others are destroyed (such as sulphurous, nitrous, and nitric acids). Under all circumstances the precipitation must take place at a moderate concentration of the acid; too highly concentrated sulphuric acid is decomposed by sulphuretted hydrogen with separation of sulphur, according to the equation

$$3H_2S + SO_4H_2 = 4H_2O + 4S;$$

the acid must therefore be in the state of chamber-acid, or, better, not above 106° Tw. When the arsenic is present as arsenic acid, it is much more slowly precipitated than when present as arsenious acid.

The simplest way might be thought to consist in generating the sulphuretted hydrogen within the liquid itself; and we shall first consider the methods and proposals made for this purpose.

(*a*) *Precipitation by barium sulphide.*—Proposed by Dupasquier in 1845, this process was carried out practically at Chessy (Hofmann's Report by the Juries, 1862, p. 12); and it appears to have been used at most of the French works where the acid is purified at all. In this case barium sulphate and sulphuretted hydrogen are formed, the latter being in the nascent state and therefore acting very energetically; this process has, moreover, the great advantage of leaving nothing soluble behind in the acid. It has been objected that the barium sulphide must be pure and must contain no thiosulphate, since otherwise the well-known decomposition between H_2S and SO_2 with separation of sulphur takes place; this, however, is unfounded, because the barium thiosulphate likewise precipitates the arsenic in the state of sulphide (see below), and only an excess of it (which ought to be avoided in any case) would occasion the above-mentioned reaction. Barium sulphide, according to H. F. Stahl, is most conveniently applied as follows:—The acid is diluted to 76° or 82° Tw., heated to 80° C., and a solution of barium sulphide of 12° Tw. is run in at the bottom of the vessel in such a manner that no H_2S escapes. The As_2S_3 is filtered off on a sand-bed, placed on a layer of quartz lumps, and thus the arsenic is reduced to 0·01 per cent. As. But as the acid, on standing in the filter, again takes up a little arsenic, it is treated with gaseous H_2S, and is thus reduced to 0·005 per cent. As, which cannot be attained either with BaS alone or with H_2S, but only by the successive application of each.

(*b*) *Sulphide of iron* may be employed in cases where the iron does no harm—for instance, for acid required in the tinning and galvanizing (zinking) of iron &c. Its application, however, is very limited.

(*c*) *Sulphide of sodium* is capable of much wider application, although it, too, introduces a foreign substance (sodium sulphate) into the acid; this, however, is innocuous for most uses of the acid. It can easily be made by reducing sodium sulphate with coal; and it must be added to the acid to be purified until no further precipitation takes place. The filtration of the precipitate will be described later on.

(*d*) *Crude calcium sulphide* (alkali-waste) can be used exactly in the same way as sodium sulphide, and with the same drawback of introducing some fixed impurities, since part of the $CaSO_4$ remains in solution.

(*e*) Thomson (G. P. 6215, 1884) employs *ammonium sulphide* for precipitating arsenic and antimony, and at the same time destroying the nitrous compounds in chamber-acid. He then filters over finely divided lead, and concentrates in the usual manner.

(*f*) *Sodium and barium thiosulphates* are very much recommended; the latter is more expensive, but leaves nothing soluble in the acid. The following is the reaction which occurs:—

$$As_2O_3 + 3S_2O_2Na_2 = As_2S_3 + 3SO_4Na_2.$$

According to W. Thorn (Dingl. Journ. ccxvii. p. 495), the sodium thiosulphate is actually used in some works. Chamber-acid of 106° Tw. is heated to 70°–80° C., and the required quantity of the reagent, either in solution or as powder, is well stirred up with it. The arsenic sulphide is separated in flakes, which soon gather into lumps and sink down to the bottom of the tank; the clear acid is drawn off; and fresh quantities are purified in the same tank, until at last there is too much precipitate collected at the bottom, when it is removed and washed. The operation is very simple; and if an excess of the reagent is avoided, very little sulphur dioxide is evolved. In a particular instance, the average percentage of arsenic in chamber-acid of 106° Tw., before purification, amounted to 0·098 per cent., afterwards to 0·004 per cent. The purified acid contains from 0·03 to 0·04 per cent. sodium sulphate, which is harmless for most purposes.

In some cases the presence of sodium sulphate in the acid is objected to, especially when the strongest acid is to be obtained. It is therefore preferable to employ barium thiosulphate, which is easily obtained by mixing moderately concentrated solutions of sodium thiosulphate and barium chloride; most of the barium thiosulphate is precipitated in a crystalline form and is separated from the worthless mother-liquor on a vacuum-filter. The acid to be purified is heated to about 80° C., and is well agitated (which can be most readily done by a stream of air), the requisite quantity of barium thiosulphate is thrown in, and the temperature is kept at 80° to 100° till all the arsenic is precipitated. The reaction is :—

$$As_2O_3 + 3BaS_2O_3 = A_2S_3 + 3BaSO_4,$$

so that nothing soluble is left in the liquid. The mixed mud of arsenious sulphide and barium sulphate settles down very rapidly; it is separated from the acid by decantation or filtration and washed in order to remove most of the acid. Where the barium sulphate is of some value, it is easily recovered by boiling the mud with milk of lime, when the arsenic is dissolved, and can be reprecipitated from the solution for sale as "yellow arsenical glass," whilst the residue of barium sulphate can be submitted to the usual treatment for the manufacture of barium chloride. This process is actually carried out on a considerable scale, but it is not quite so cheap as the treatment with sulphuretted hydrogen, and does not seem adapted to acids containing a large quantity of arsenic.

(*g*) *Precipitation by gaseous hydrogen sulphide.*—This process appears first in a patent by W. Hunt (No. 1919, of 1853) and is that which is most usually employed on a large scale.

The older, now obsolete, processes used at Oker and Freiberg are described and illustrated in our first edition, pp. 469 to 473: comp. also Knocke, Dingl. Journ. cliv. p. 185; Wagner's Jahresb. 1859, p. 145. We will here give only the results of Schnedermann's analyses of the acid before and after purification :—

(α) Impure acid contained in 10,000 parts—

Specific gravity.	Arsenious acid.	Lead sulphate.
1·832	11·86	3·74
1·837	13·19	2·85
1·836	14·21	5·21

(β) After purification, in 10,000 parts—

SO_3	7749·10
H_2O	2243·54
$PbSO_4$ (with traces of $CuSO_4$)	1·72
Na_2SO_4 and K_2SO_4	1·35
$CaSO_4$	0·58
$FeSO_4$	2·91
As_2O_3	0·31
H_2O_3	0·49

The acid was perfectly free from nitrogen compounds. Subsequently, according to Kerl, acid has been obtained containing no more than 3·15 As_2O_3 and Sb_2O_3 together and 11·28 $PbSO_4$ in 100,000 parts.

According to official information obtained by me from the Freiberg Mining Office, the original percentage of arsenic in the ores burnt there averages 2 to 2·5 per cent. As. 97 per cent. of this arsenic is condensed as flue-dust, and about 3 per cent. gets into the chamber-acid, which before purification usually contains 0·02, exceptionally up to 0·08 per cent. As (1902). It is employed in this state in the Gay-Lussac tower or for the manufacture of superphosphate. All other acid is purified, as described below, and then contains only 0·0002 per cent. As_2O_3.

The precipitating-process used at the Freiberg and many other works is described at great length by Bode (Dingl. Journ. ccxiii. p. 25; Wagner's Jahresb. 1874, p. 259); the following is an abstract of this, together with some notes I have recently obtained from Freiberg and taken from actual practice in other places *.

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* According to official information obtained by me the apparatus and processes described in the text were still at work in 1890, and they would appear to have also been in use in 1902; but a different process, hitherto kept secret, is followed at Aussig.

1. *Generation of sulphuretted hydrogen.*—For this purpose a matte is smelted, consisting principally of ferrous sulphide, FeS, in which at the same time the silver contained in the crude ore is concentrated to the amount of one third of the original weight. The work was formerly done in a blast-furnace (comp. our second edition, p. 643). Now (1902) the ferrous sulphide is made in a reverberatory furnace, where per 24 hours three or four batches of the following composition are charged: 28 cwt. pyrites (lumps), 8 cwt. old lead slags containing 30 per cent. silica, and 3 cwt. limestone. The consumption of coal is about 4 tons (of good quality), the yield of matte (essentially FeS) is on an average 2½ tons per day.

The matte is broken up into pieces about the size of a fist, and put into the sulphuretted-hydrogen generators; these receive 4 to 5 tons at a time, which last 8 to 10 weeks. Then weak sulphuric acid of 55° to 77° Tw. is added, such as is obtained in washing the arsenic sulphide; later on, the acid may go down to 32° Tw. Each apparatus daily receives 5 cwt. acid of 32° Tw. From 5 tons of matte 7¼ tons of crystallized sulphate of iron are obtained, the manufacture of which from the weak lyes takes place in the usual manner. The generators are represented in figs. 322 to 329 (pp. 794–795). They are wooden tanks A and B, made of 3½-inch planks lined with lead and connected by a lead tube *a*. The tank A (5 feet 6¾ inches square and 5 feet 2 inches deep) is charged with matte after lifting off the cover, or through the manhole *b*; an india-rubber washer is then put in, and the cover is tightened by thirty screw-bolts. The acid is run in through a pipe in the cover. B also has a cover, but without an india-rubber joint, as it has only to receive the solution of ferrous sulphate forced over by the pressure of the gas in the washing-apparatus (figs. 328 & 329) and the regulating-valves, just as is the case with the ordinary laboratory apparatus. The tank A is very strongly bound with iron, which is leaded all over. Steam-pipes, *e*, prevent the ferrous sulphate from crystallizing; *f* serves for running the liquor off. On the bottom of A radially-placed fire-bricks form a grate (fig. 324), upon which a lead sieve *g* (fig. 323) is laid; and the matte lies upon the latter. The lateral manholes *h* permit raking out the residue containing silver. For each 5 tons of chamber-acid on an average 1½ cwt. of matte is consumed.

2. *Precipitation of the arsenic.*—The chamber-acid of 106° Tw. is

treated with H_2S without dilution or heating. The apparatus easily purifies 15 tons of acid daily by a single treatment. It is represented in figs. 330 to 336 (p. 797). It consists of a square tower of 5 feet 4 inches × 5 feet 6⅝ inches section, and 16 feet 3 inches available height, which is constructed in the well-known manner with a wooden framework and lead sides of 10 lb. to the square foot. The sulphuretted hydrogen enters at the bottom; the air carried along with it and the steam escape at the top. The tower is filled with 24 tiers of A-shaped inverted lead gutters, 5½ inches high and as wide at the base, made of 10-lb. lead; the lower edges of the gutters have indentations of a tolerably small pattern (fig. 336). Owing to this, the acid cannot run down in jets, but only in single drops, which, in falling upon the next lower gutter, squirt about and present a large surface to the gas. In each tier there are nine gutters, so arranged that the passage between each two of them corresponds to the upper edge of the gutter in the next lower tier. They are 3 feet 3 inches long, and laid loosely on leaded ledges on each side, with 1 inch hold on the latter; their vertical distance is 7 inches; the distance between the tiers, therefore, 1½ inch. The acid runs in at the cover *l* through nine lead pipes with funnels and regulating-cocks just over each of the lead gutters; there is a hydraulic lute and an oscillating bucket, the details of which are shown in figs. 335 & 336. The lead gutters should not be burnt fast in the tower, as lumps of arsenic sulphide occasionally get jammed between them. These can sometimes be melted and removed by letting in steam.

The strength of 106° Tw., as indicated by Bode, is rather too high for speedy and complete dearsenication; it is preferable to take the acid only 100° Tw. strong. The process is hastened by employing a slight pressure in the precipitating-tower. This is easily done by not allowing the gas to escape from the top of the tower directly into a chimney, but passing it through a few inches of water, or, preferably, milk of lime, which retains any H_2S not absorbed in the tower.

Of course constant tests must be made to ensure complete purification in this tower. For ordinary purposes it is sufficient to employ a simplified Marsh test as follows:—Put some of the acid into a four-ounce bottle, closed with a cork, provided with an outlet-pipe drawn out to a point. A piece of pure zinc is dropped in, the cork is inserted, the gas issuing is lighted (with the ordinary

Fig. 322.

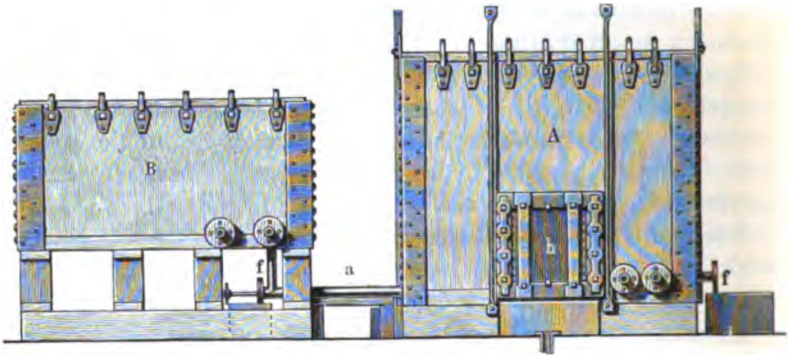


Fig. 323.

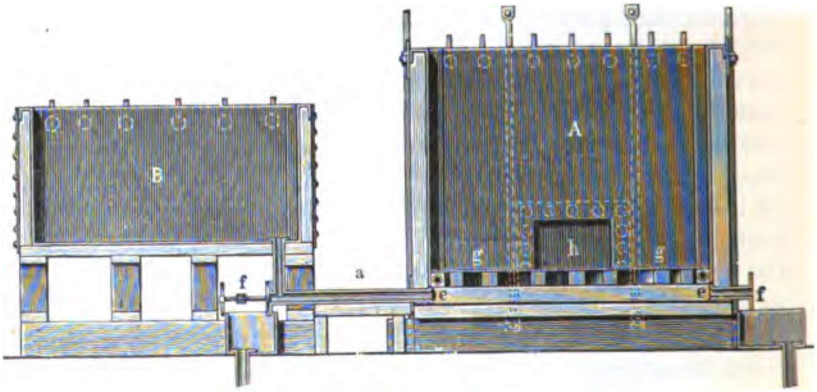


Fig. 324.

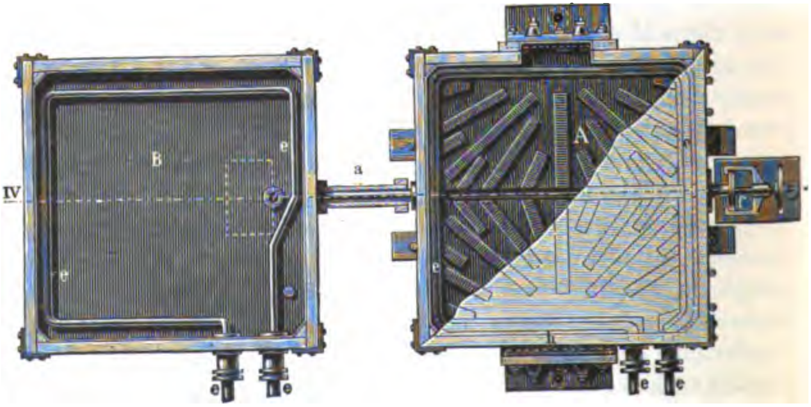


Fig. 325.

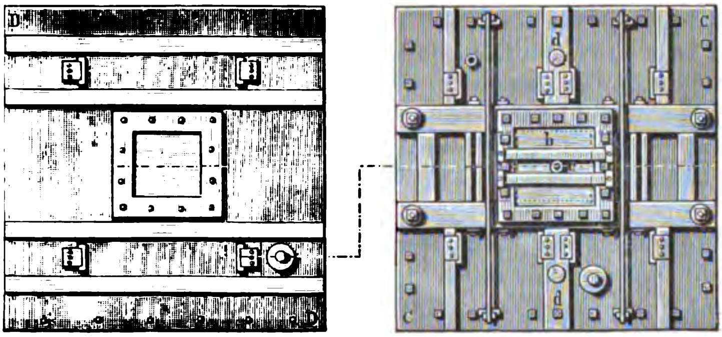


Fig. 326.

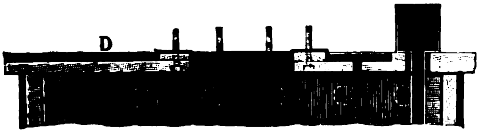


Fig. 327.

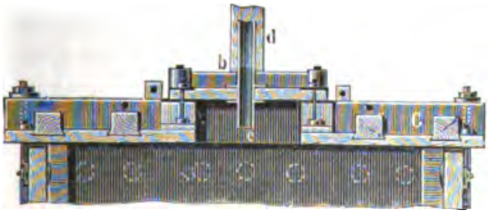


Fig. 328.

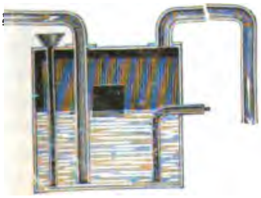
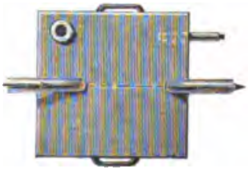


Fig. 329.



precautions against an explosion by premature lighting if the gas contains air) and the flame is directed on a slab of porcelain, where no spot of As should be produced. For more accurate observations the methods mentioned *supra* p. 248 and those to be noticed in the Appendix should be employed. If a batch of acid is not found free from arsenic by the above test, it must be pumped up and treated once more. This test should be repeated by the laboratory chemist before passing a batch as purified, and in cases of any importance the acid should be tested a third time before being sent out. The above simple Marsh test, or the ordinary Marsh-Berzelius test (heating the gas in a tube, where metallic arsenic is deposited), does not detect the minutest traces of arsenic; but it may be taken that any acid in which these tests do not indicate any arsenic is "practically" free from arsenic and can be used for all purposes, like acid made from brimstone *.

3. *The filtering and washing of the arsenic sulphide* is a somewhat troublesome operation. At Freiberg, for this purpose a vacuum-filter is used, which is shown in figs. 337 to 339 (p. 798). A is the vacuum-retort, B the filtering- and washing-vessel. The former is a small, second-hand steam-boiler of 1 foot 10 inches diameter and 5 feet 7 inches length. Steam is conveyed into it through *a* from a boiler ; through *b* the air goes away along with the condensed water; and the cock there is only shut when steam has passed through for several minutes. Then *b*, and afterwards *a*, are shut, and the boiler is allowed to cool for some time in order to condense the steam. Then the cock *c* is opened, which connects the vacuum-retort and the space below the filtering-layer in the box B. This box has already been filled with the acid to be filtered, whose level is always kept at the same height, lest any cracks be formed in the exposed layer of arsenic sulphide, through which air would enter and destroy the vacuum. By several times shutting *c*, opening *a* and *b*, driving out the air by steam, and

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* This is universally done, even for the purpose of manufacturing articles of human consumption, in France, Germany, and most other countries, where no brimstone whatever has been used in the manufacture of sulphuric acid for many years past. No inconvenience seems ever to have been caused by this practice in these countries; but since the "beer-scare" of 1900 many people in England demand that no acid should be allowed to be used in the manufacture of articles of food &c. except that made from brimstone.

cooling down the boiler A, a vacuum of from 10 to 12½ lb. may be obtained. [Probably less steam and labour would be expended

Fig. 330.

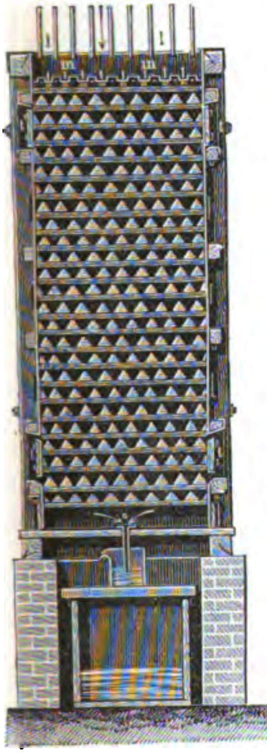


Fig. 331.

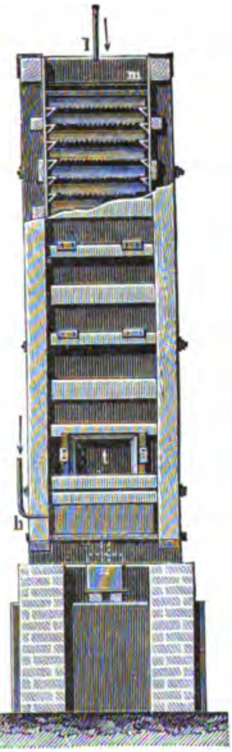


Fig. 332.

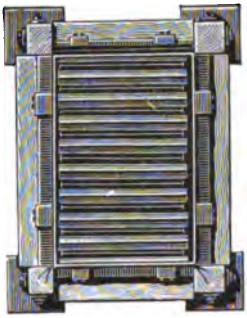


Fig. 333.

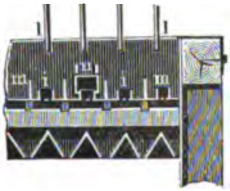


Fig. 334.

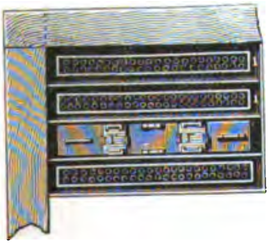


Fig. 335.

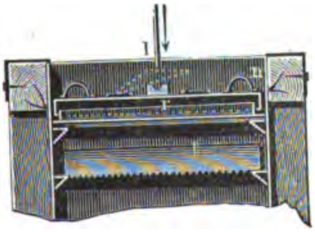


Fig. 336.

if an air-pump were used.] The same vacuum-retort [or air-pump] may work several filters, which can be filled, washed, &c. at will, since the cock *c* permits isolating every one of them.

The filters B are made of 2-inch planks, strengthened at the bottom at *e*, fig. 339, lined with lead, 4 feet 4 inches × 5 feet 7 inches section and 1 foot 10 inches high. A double pavement of acid-proof fire-bricks leaves a gutter, communicating with the burnt-on pipe *l*. This ends in an intermediate vessel C, whose cover is provided with connecting-tubes for the pressure-gauge *o*,

Fig. 337.

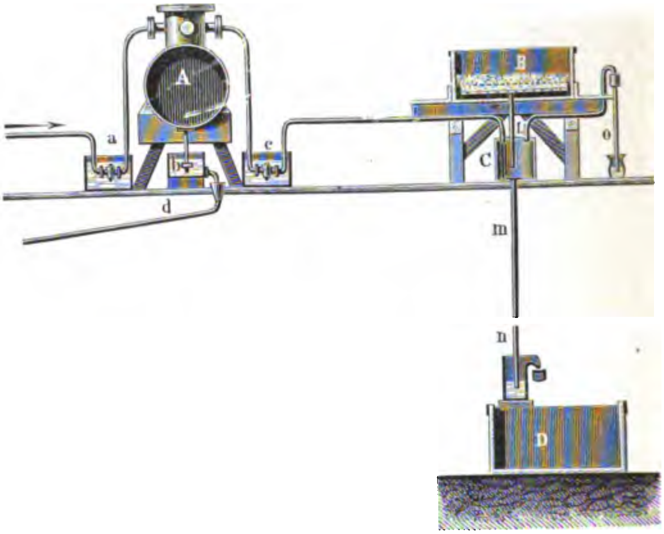


Fig. 338.

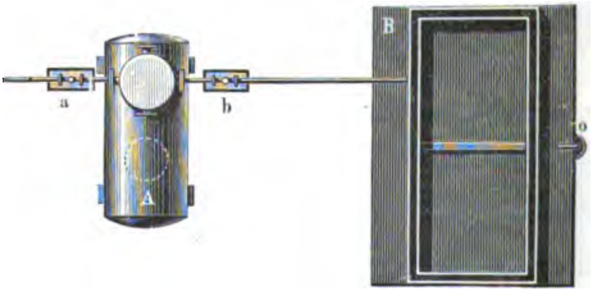
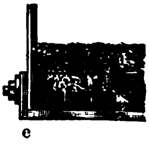


Fig. 339.



and the vacuum-retort A, at *c*; *mn* takes the acid to the receiving-tank D; but the pipe *mn* must be longer than the height of a column of water forced up by the atmospheric pressure, lest the acid should run over into *c*. Over the fire-bricks in B is placed a layer *n* of broken-up quartz (fig. 339)—pieces the size of a walnut at the bottom, and of finer grain higher up; over this there is a finely perforated sheet of lead, and on the top a layer of powdered arsenic sulphide; the whole filtering-stratum rises 11½ inches above the bottom of the vessel. Where the acid runs in, a piece of lead is placed so as to keep the top layer from being damaged. Every two or three weeks the layers *n* and *m* and the perforated lead plate must be taken out, and the quartz pieces as well as the arsenic sulphide must be rinsed in water. The whole plant requires several pressure-apparatus (acid-eggs) and a good air-pump.

At Oker the work is done very much as at Freiberg (Bräuning, Preuss. Zeitsch. &c. 1877, p. 142); but at the former place only that portion of the acid is purified which is not sold to large consumers, especially for superphosphate-making. It is there thought best to dilute the acid to 97°–100° Tw. (comp. p. 793) and to assist the generation of sulphuretted hydrogen by injecting steam at the beginning.

An English patent of M'Kechnie and Gentles (No. 3229, 25th August, 1877) contains essentially the same process as is practised at Freiberg and Oker.

Mr. G. E. Davis informs me (1902) that at his works the following process is used for dealing with the arsenious sulphide obtained in purifying O.V. The mud is warmed up to the melting-point of naphthalene, paraffin, &c., and a little of these substances is added and the mixture well stirred. Afterwards the naphthalene may be distilled off by steam; if paraffin is used, this may be separated by treatment with ammonium sulphide, or in various other ways.

Riley and Barnes (B. P. 25,444, 1901) recover arsenious acid from the arsenious sulphide by heating it to about 160° C. with nearly its own weight of strong sulphuric acid for some hours. The floating scum of sulphur is removed and washed, and the acid liquor is concentrated to obtain crystallized arsenious acid.

Falding (Min. Ind. viii. p. 583) describes the American practice, where lead-lined boxes are placed in front of a Freiberg tower, as shown in figs. 330 to 336 (p. 797). The H_2S gas is forced through the acid in these boxes by means of a perforated pipe on the bottom and only enough acid is run down the tower to prevent the escape of any of the gas. The pipes are connected in such a manner with the boxes that the gas can be made to pass through any one of the boxes first, and that any box can be disconnected from the series. The box so cut out is allowed to rest for a day or two, and the As_2S_3 is settled out so completely that ¾ or more of the supernatant acid can be decanted without any further treatment. The remaining sludge of As_2S_3 and acid is filtered through broken quartz of graduated sizes in leaden boxes. [This plan requires pumping H_2S against pressure, instead of pumping the acid; the former is probably more expensive than the latter. But the collecting and filtering of the As_2S_3 is undoubtedly less troublesome than in the Freiberg tower.]

Leroy W. McCay (Chem. Ind. 1889, p. 371) proposes facilitating the precipitation of arsenic by H_2S, by conducting the operation at 100° under pressure and with agitation. [Such a process, excellent as it may be for the laboratory, is far too troublesome and costly for a manufacturing scale.]

Kupfferschläger (Bull. Soc. Chim. xliv. p. 353) dilutes the acid with its own volume of water, treats with SO_2 in order to reduce any arsenic or nitric acid to arsenious or nitrous acid, and then passes H_2S through, which causes all As, Pb, and Se to be precipitated. This proposal he repeats, without any change whatever, in Monit. Scient. 1889, p. 1434.

The evolution of sulphuretted hydrogen, where no such matte (FeS) as made at Freiberg is obtainable, can be produced cheaply with soda-waste, where an alkali-works is near. Hartmann (G. P. 9275) produces this gas by passing pyrites-kiln gas through a cupola-furnace filled with red-hot coke. When the temperature has fallen, the current of SO_2 is interrupted and air is blown into the coke till the heat rises again. Or else the impure SO_2 is mixed with the vapours of hydrocarbons and passed through a red-hot retort.

At an American works I found H_2S prepared for the above object from dilute sulphuric acid and sodium sulphide manufactured for this purpose.

Whitehead and Gelstharpe (Engl. pat. 18,940, 1894) obtain H_2S for this purpose by treating liquid from partially oxidized vat-waste with HCl. The mixture thus evolved, containing H_2S, SO_2 [!], and atmospheric air, is said to act better than pure air. [This process is not patentable. The employment of vat-waste for this purpose has been expressly mentioned in this connexion in my Treatise which appeared in 1891 (comp. p. 800); nor is the partial oxidation patentable, since vat-waste, such as would be available, always has been, and always will be, partially oxidized; nor is it essential whether the waste itself, or the yellow liquor draining from it, is employed. The assertion that SO_2 occurs in these gases at the same time as H_2S is of course wrong, since it is not the question of mere traces. The apparatus described by the inventors presents no specially remarkable features.]

A very curious observation has been made by a chemist whose trustworthiness I can in no way doubt, although I have never heard of the subject elsewhere. If the treatment with gaseous hydrogen sulphide is continued to the point that the last trace of arsenic is precipitated [in which case much free H_2S must be present], the acid cannot be boiled down in lead pans without risk of destroying them. Sometimes, not always, this takes place when the concentration reaches spec. grav. 1·63. First a white crust is formed at the line where the acid and the air meet; this eats further down and suddenly the pan falls to powder. If after noticing the first signs the pan is emptied, washed out, and used as a " weak " pan, this will do; but when used as a " strong pan " the destruction goes on even with ordinary acid. [This behaviour reminds one of the sudden conversion of metallic tin into a grey powder which is sometimes observed. Where Kessler ovens are employed for concentrating the dearsenicated acid, comp. Chapter IX., the above inconvenience will not be felt.]

The cost of treating a ton of acid for the removal of arsenic may be taken at about 5*s.* if the ferrous sulphide &c. has to be bought and the by-products are not utilized. It may be considerably reduced by making ferrous sulphide as above described, or employing some other cheap source of H_2S, and by utilizing the ferrous sulphate formed in the process; and if the arsenious sulphide can be sold to advantage, there may be even a slight profit in the purifying operation.

Notoriously much of the acid sold in England as "brimstone acid" is not made from brimstone, but from spent gas-oxide or from pyrites, and is merely dearsenicated in the latter case by sulphuretted hydrogen as described above. Of course this treatment also removes all nitrogen compounds, lead, selenium, copper, &c.,

so that this acid, if properly purified, is really purer than real brimstone acid, except, of course, as regards iron. The acid coloured brown by the previous processes (especially where the Gay-Lussac tower has been packed with somewhat soft coke) is rendered much lighter in colour by the precipitation of the arsenious sulphide.

For electrical storage-batteries sulphuric acid should be as free from arsenic as possible. Arsonval endeavours to attain this by pouring 4 or 5 c.c. of colza oil on to a litre of sulphuric acid, which is to form glycerine-sulphuric acid, and to precipitate the arsenic, lead, &c. in the form of soaps [?]. Gothard prescribes the same addition; the mixture is to be shaken up, allowed to stand for 12 hours, poured into water, and, after cooling, the sticky mud must be skimmed off the purified acid (Chem. Zeit. 1892, p. 163).

Purification of the Sulphuric Acid from Nitrogen Compounds.

Already, when treating of the purification of sulphuric acid from arsenic, it has been stated that mostly by the same operation the nitrogen compounds are removed, and this is always the case when sulphuretted hydrogen is employed for that purpose. In most works, however, no such purification from arsenic takes place; and for most uses of the vitriol the small proportion of nitrogen compounds which it contains is so unimportant that their removal is not called for. In all cases, however, where sulphuric acid has to be concentrated in platinum apparatus it must be purified as much as possible from nitrogen acids, as otherwise the platinum, as will subsequently be described, would be much more strongly acted upon.

1. *Purification by sulphur dioxide.*—Payen has proposed a contrivance for this object. This is a cover over the first boiling-down pan, provided with partitions which force the gas to travel twice backwards and forwards, and below which the sulphurous kiln-gas circulates. Some manufacturers, instead of this, use pans arched over. This apparatus, however, fulfils its purpose very inefficiently, because the contact between the acid and the sulphur dioxide is very incomplete. The latter object can be attained perfectly in all works where a Glover tower is employed; in this the acid can be fully denitrated and, moreover, a small quantity of sulphur dioxide can be dissolved, in which case, as Scheurer-Kestner

has shown (see Chapt. IX.), it acts least upon platinum; but, unfortunately, the Glover-tower acid, owing to its large percentage of iron, cannot well be used for concentration in platinum stills.

At some works they arrange a small preliminary chamber (tambour) in which there are bottom partitions open at opposite ends, so that the acid entering from the next (large) chamber has to travel a circuitous route long before it arrives at the place where it is drawn off for use. This is done with the object of completely taking the nitre out of the chamber-acid and making it sulphurous, the fresh burner-gas acting upon this acid with full force. Such acid is then employed for concentration in platinum stills. The object of completely removing the nitre (and together with it the selenium) is still better attained by blowing kiln-gases by means of an injector right through the acid in a finely divided stream, and allowing the deposit to settle down by running the acid in circuitous channels.

2. *Treatment with brimstone* has been proposed by Barruel. It is used in the shape of flowers of sulphur, which sometimes, according to Schwarzenberg, is put into boxes of stoneware placed in the first pan, in which the temperature does not rise to the melting-point of sulphur, and in which the acid contains most water. Special care must be taken that no sulphur gets into the following pans, because strong hot sulphuric acid is decomposed by sulphur with the formation of SO_2, and for each part of S 6½ parts of SO_4H_2 are lost. According to Bode ('Gloverthurm,' p. 3) this process is not efficient; so long as the brimstone is still in the state of powder its action is very slight, although the lead is already being acted upon by the nitrogen acids. Later on, with the rise of temperature, the brimstone melts and rises in small drops to the surface of the hot acid, whence it mostly escapes into the air as SO_2.

3. *Treatment with organic substances.*—*Oxalic acid* has been proposed by Löwe. *Sugar* has been suggested by Wackenroder. Skey recommends agitation with *charcoal,* but only for dilute acid (Chem. News, xiv. p. 217). Olivier uses a little alcohol in the lead pans ('Rapports du Jury international,' 1867, vii. p. 35).

4. *Ammonium sulphate* has been proposed for this object by Pelouze (Ann. Chim. Phys. lxvii. p. 52), and has been proved to be the best of all reagents. By this the nitrogen acids can be so completely removed that the vitriol is tinted red by the first drop

of a solution of potassium permanganate. In this case nitrogen escapes, according to the following equations:—

$$N_2O_3+2NH_3=3H_2O+4N,$$
$$2SO_5NH+2NH_3=2SO_4H_2+2H_2O+4N,$$
$$3NOH_3+5NH_3=9H_2O+8N.$$

This substance is now universally employed for acid to be concentrated in platinum stills. Under normal conditions 0·1 to 0·5 lb. of ammonium sulphate suffices for purifying 100 lb. of vitriol.

It appears as if the addition of ammonia was sometimes carried to a ridiculous excess; for Gintl (Wagner's Jahresb. 1880, p. 259) found, in so-called "chemically pure" sulphuric acid, 5 per cent. of NH_3.

Pattinson (J. Soc. Chem. Ind. 1889, p. 706) recomends the treatment with ammonium sulphate for the sulphuric acid employed for generating carbonic acid in the manufacture of aerated beverages, as an extremely small quantity of nitrous acid (0·026 per cent. of N_2O_3)causes the beverage to be turbid, and destroys the pungency of the ginger essence &c.

Lunge and Abenius (Zsch. f. angew. Chem. 1894, p. 609) show that *nitrous acid* (*i. e.* nitrososulphuric acid) is very quickly destroyed by boiling with a proportion of ammonium sulphate of 1 NH_3 to 1 acid nitrogen; even with sulphuric acid of 140° Tw. this takes place in five minutes. But *nitric acid* is far more stable; it requires half an hour's boiling with its equivalent of ammonium sulphate, in the case of the strongest sulphuric acid, for its destruction, and many hours' boiling with a large excess of ammonium sulphate in the case of acid of 140° Tw. Hence any contamination with nitric acid must be carefully avoided if the sulphuric acid is to be concentrated in platinum, since some HNO_3 will get into the platinum still in spite of all precautions; but nitrous acid is easily removed at every stage by ammonium sulphate.

Purification of Sulphuric Acid by special methods (by electrolysis &c.).

According to Journ. Franklin Institute, v. p. 65, lead, iron, and arsenic can be removed by subjecting the sulphuric acid to electrolysis.

Askenasy (Germ. pat. 86,977) subjects sulphuric acid for some time to electrolysis and allows the products to act upon the acid.

Among these is ozone, which destroys organic substances and hydrochloric acid (with formation of chlorine); finely divided sulphur, which reduces the nitrogen compounds; and hydrogen sulphide, which acts in the same manner and also in precipitating any metals present. The latter takes place only with *concentrated* acid. The electrolysis is carried out at ordinary or slightly elevated temperatures, with lead electrodes without diaphragm, and with agitation of the liquid, beginning this after the current has acted quietly for some time. The current-density should be 1 or 2 amps. per square decimetre and the tension 6 volts. After a few hours the acid is colourless; it is then heated up, if necessary, in order to agglomerate the preciptate, or else diluted and afterwards filtered.

Teed (E. P. 17,612, 1887) proposes to remove the *lead* from sulphuric acid by means of hydrochloric acid.

Nicklès removes *hydrofluoric acid* from sulphuric acid by diluting this with twice its volume of water and heating for 15 hours, replacing the water as it evaporates.

Coloured Acid.

A *brown* colour is so frequently found in sulphuric acid up to about 80 per cent., that the designation "brown oil of vitriol" (B.O.V.) has become universal in England for acid of about 140° Tw. This colour is destroyed during the higher concentration of the acid, and also by the treatment with sulphuretted hydrogen (p. 790), but not always entirely.

Nörrenberg (Chem. Ind. 1890, p. 363) points out that the *red colour* sometimes found in commercial sulphuric acid of about 140° Tw. may be formed by the contact of that acid, when containing a slight quantity of nitrous acid, with iron tanks. The iron, acting upon the nitrous acid, generates nitric oxide, which is dissolved in the ferrous sulphate formed—thereby producing the red colour. Oxidizing agents discharge this colour by converting the ferrous into ferric salt, and the NO into N_2O_3. Completely denitrated acid never assumes the red colour when kept in iron tanks, nor does stronger acid ("rectified oil of vitriol"), which has much less action upon the iron. The same colour may be produced in the small chambers or "tambours" sometimes placed before the first large chamber; here the sulphuric acid is still predominant, and iron is present as flue-dust, so that the conditions are present for the formation of a solution of NO in

$FeSO_4$. The main chambers, where nitre predominates, never show that colour, as here all the iron must be present as ferric sulphate.

In many cases it is decidedly *selenium* in the free state which causes the red colour. This will occur if selenious acid is reduced to Se by SO_2 in the Glover tower or in the chambers. The most usual proceeding is to convert the Se into SeO_2, and thus to remove the colour by adding a little nitric acid, which, however, cannot be done without employing an excess and thus introducing another objectionable substance. Le Roy (Monit. Scient. 1901, p. 406) therefore prefers to add a sulphuric-acid solution of potassium or sodium permanganate, of which at most 10 grams is necessary for a ton of acid. Any pink colour remaining is destroyed by oxalic acid. The temperature employed is 50° or 60° C.

A very deeply coloured kind of acid is the *acid-tar* or *sludge-acid*, which will be described more fully in Chapt. IX. It is the residue from the acid treatment of mineral oils.

Waring and Breckenridge (U.S. P. 643,578) purify this acid-tar by mixing with it, at low temperatures, sodium nitrate in just the quantity required to effect the purification.

The colour of waste acid from *nitrating operations* (nitroglycerine, gun-cotton, nitro-benzene, &c.) may also be very strong, but this acid is never sent into trade. It is usually denitrated at the works where it has been obtained, where the colour remaining in the recovered sulphuric acid is of no consequence.

Production of chemically pure Sulphuric Acid.

Hayes (Dingl. Journ. cx. p. 104) proposed to add nitre to sulphuric acid of 152° Tw., coming from the lead pans, sufficient for destroying the largest portion of any hydrochloric acid present, and for oxidizing completely the sulphurous and arsenious acids, then to destroy the nitrous acid &c. again by adding $\frac{1}{8}$ per cent. of ammonium sulphate—to add a little oxide of lead, to allow it to settle in leaden vessels, and to cool the clear acid siphoned off in shallow lead pans down to $-18°$ C. In this case the hydrate $SO_4H_2 + H_2O$ crystallizes out; the mother-liquor containing all impurities is decanted; the crystals are washed with pure acid, and then form square prisms, sometimes an inch thick and $1\frac{1}{2}$ inch long. These are fused in clean lead vessels and used as they are, or further concentrated in a platinum still. This process was intended to save the distillation; it has not been successful, however; for it is troublesome and yet does not produce a really pure acid. Exactly the same plan has been proposed by Tjaden-Möddermann (Zeitschr. f. analyt. Ch. 1882, p. 218; Fischer's Jahresb. 1882, p. 260).

The only plan for making perfectly pure sulphuric acid for pharmaceutical and analytical purposes is still *fractional distillation,* connected with such operations as previously remove the volatile impurities of the vitriol or convert them into fixed compounds. We have seen (pp. 782 & 802) how the arsenic and the nitrogen compounds can be removed. We may destroy the latter first by ammonium sulphate, and convert the arsenious acid into non-volatile arsenic acid, or else add a little common salt and reject the first distillate, which contains all the arsenic as $AsCl_3$. It is safer, on account of the danger of spurting, first to remove both nitrogen compounds and arsenic by means of sulphuretted hydrogen; but then the acid must be much diluted previously. It never becomes absolutely free from arsenic in this way; it is therefore preferable to employ brimstone-acid for retification.

According to Nicklès, *hydrofluoric acid* can be removed by diluting it with twice its bulk of water and heating it for 15 hours (comp. p. 805).

The fixed substances, such as iron, lead, copper, &c., remain in the retort on rectifying; and in order to avoid contamination with organic substances, the receiver is changed when about $\frac{1}{20}$ part of the acid has come over; the distillation is interrupted when only $\frac{1}{8}$ to $\frac{1}{10}$ of the acid is left behind. The portion distilling between these two limits is quite pure.

The distillation of sulphuric acid in glass retorts is a very disagreeable and even dangerous operation, on account of the strong *bumping* caused by the sudden development of large bubbles of vapour; this is especially favoured by the lead sulphate separating. In such cases the retort is sometimes bodily lifted up, and of course smashed when it falls back upon its seat. The bumping must therefore be avoided as much as possible, for which purpose the following plans have been proposed.

Berzelius prescribed heating the retort more from the sides than from below, by placing a sufficiently wide sheet-iron cylinder upon the grate of the furnace, so that the bottom of the retort just fits into it; the coals in the furnace then only heat its sides. In this case, however, the iron cylinder may act as a cracking ring; and A. Müller (Polyt. Centralbl. 1860, p. 1069) therefore employs an iron pan, in whose bottom a special iron ring protects the retort-bottom from heating, whilst the remaining space of the pan round the retort is filled with fine cast-iron borings. Sometimes the retort is heated in an iron vessel just fitting it, which is generally filled with sand; Reese (Dingl. Journ. clv. p. 395) puts ashes on the bottom, as a bad conductor of heat. Frequently, however, the retort is heated direct in a fire, and is merely protected by asbestos or by a paste of clay which is continued up to the curve of the neck, so that the vapour is prevented from condensing too soon.

In any case the retorts must be made of very good glass, free from knots, equally thick all over, and not too large; the neck must be protected against draughts, and must not extend to the middle of the receiver, as the latter might be cracked by the hot drops of acid falling into it. It is neither necessary nor advisable to cement the joint between the retort and the receiver, or to cool the latter, considering the high boiling-point of the acid; but it is useful to place a strip of asbestos between the neck of the retort and the receiver, in order to protect the latter against overheating at the point of contact.

The bumping is very commonly avoided by putting in substances which favour a regular evolution of vapour. For this purpose the following are useful:—platinum scraps or wire, for instance in the shape of spirals; bits of quartz, of porcelain, or of very hard coke. Pelloggio recommended a wide glass tube, drawn out to a fine point at the lower end, and reaching almost down to the bottom of the retort; through this the air can communicate with the interior (Polyt. Centralblatt, 1868, p. 392). Hager has tried this and found it useless. Dittmar conducts a continuous slow current of air through the boiling acid (see above, p. 114); this expedient has answered very well in my own laboratory.

When distilling about 1 cwt. at a time, it takes from 5 to 6 hours of moderately strong heating before the contents of the retort begin to boil; after 12 hours one twentieth has distilled off. The receiver is now changed; after 36 hours (counting from the commencement) the acid is distilled off within one eighth or one tenth, and the operation is stopped. According to whether the first change of receiver has been made a little sooner or later, acid more or less concentrated is obtained.

The following method is highly recommended, because the danger of handling such large quantities is thereby avoided. A small tubulated retort holding from a pint to a quart is employed; above this, a little to one side, a bottle of convenient size is mounted, provided with a glass tap, into which the sulphuric acid to be rectified is put, after it has been freed from all volatile impurities by previous heating. The distillation is now started in the small retort, which is about half filled, and into which a few scraps of platinum are put. Afterwards, by means of the glass tap and of a finely drawn-out glass tube, as much acid is allowed to run continuously from the stock-bottle into the retort as is distilling off. The operation may be continued till too large a quantity of fixed substances is accumulated in the retort. I have seen this plan at work on a small scale in English factories.

Pure sulphuric acid is now attainable in commerce at such a low price that it could not be produced by any of the just described means. It is in reality manufactured from the weak acid distilling over in the production of rectified O.V. (comp. next Chapter), which is concentrated by evaporation in glass retorts, or preferably in a small platinum still, to the point required.

If acid of 98 p. c. H_2SO_4 is manufactured by concentrating in iron retorts or otherwise, the acid distilling over from the retorts is often of the proper strength of "rectified O.V." (on the Continent and in America = 66° Baumé), viz. 93 to 93·5 p.c. H_2SO_4. If the arsenic has previously been removed, the *distilled* O.V. will be practically pure acid.

In England the designation "rectified oil of vitriol" (R.O.V.) or "distilled oil of vitriol" (D.O.V.) is commonly used, not for distilled sulphuric acid, but for acid concentrated by evaporation to 93 p. c. O.V. = 168° Tw.

CHAPTER IX.

THE CONCENTRATION OF SULPHURIC ACID.

Sulphuric acid, as obtained direct in the chambers (that is to say, from 106° to at most 124° Tw. strong), is sufficiently concentrated for many technical purposes; and where the acid is used up again for such purposes at the same works its further concentration is, of course, out of the question. This is the case, for instance, with large industries having their own vitriol-works, with the manufacturers of superphosphate and of sulphate of alumina (concentrated alum). Even for making sulphate of soda from common salt it is possible to manage with acid of 124° Tw., although stronger acid is decidedly preferable; and in fact some alkali-makers (not so many now as formerly) work without any concentrating-apparatus, making their chamber-acid as strong as possible. The want of concentrating-apparatus formerly excluded the application of a Gay-Lussac tower; and many works certainly did not possess such a tower. With the introduction of the Glover tower the state of things was changed, inasmuch as the manufacturers using this tower can concentrate all their acid to 144° or even 152° Tw. without any cost, and thus arrive at the same point as those who, not using that tower, concentrate their acid in lead pans. But since Glover towers are not universal, and they are also not suitable for all the uses of sulphuric acid (see p. 673), we must here describe the other concentrating-apparatus as well. These come into use especially where the strongest oil of vitriol is to be made, for which the Glover-tower acid is not very well adapted.

When boiling dilute sulphuric acid the escaping vapour consists entirely of water, and contains practically no sulphuric acid. The acid remaining behind will therefore become more and more concentrated, without any material loss of acid, so long as 144° Tw. is not exceeded. Walter (as quoted in Bode's 'Glover Tower,' p. 17) found that the loss in concentrating acid in open pans up to 144° Tw. only amounts to 0·01 per cent. At the same time the boiling-point, which in the case of chamber-acid is about 147° C., gradually rises: that of acid of 144° Tw. is 200°; that of acid of 152° Tw., 215°. Beyond this the boiling-point rises very rapidly, and finally becomes stationary at 338° C., at which point not real sulphuric acid (SO_4H_2), but an acid containing about 1·2 to 1·5 per cent. of water remains behind (p. 173). In practice this limit is hardly ever reached; the heating is stopped when the remaining acid nominally shows 168° Tw.; often its real density amounts to only 1·830 or 1·835 = 166° or 167° Tw. A table of the boiling-points of sulphuric acids, according to their dilution, has been given above (p. 193).

The way in which sulphuric acid is to be concentrated is modified, first, by the *material of the concentrating-vessels*. From what has been said above (p. 206 *et seq.*) it follows that sulphuric acid of 144°, or even up to 152° Tw., acts very little upon lead, even when hot; and so long as the acid has not to be stronger than 144° Tw., *leaden vessels* are nearly always used, which offer the advantage that they can be made of any size, and that when they are worn out they can be very easily melted down and the material used over again. It is not advisable to carry on the concentration in lead pans above 144° Tw., because at that point the lead is much acted upon; and in no case can lead pans be used beyond 152° Tw., both because in that case the boiling-point of the acid too nearly approaches the temperature at which the lead begins to soften, and because the acid then acts too strongly upon it.

The *quality of the lead* used for boiling-down pans is of great importance; this subject has been treated p. 206 *et seq.*

The further concentration of the acid must take place in vessels of glass or platinum, or in apparatus of peculiar construction, which will be subsequently described.

The concentration of sulphuric acid to 144° *or to* 152° Tw. is therefore always carried on in *lead pans* (apart from the Glover tower). These pans, however, may be constructed in very different ways. They may either be heated by a direct fire, and either from the top or from the bottom, or by steam, or by the waste heat of the pyrites-burners; and their construction differs accordingly, as will appear from the detailed description.

1. *Lead Pans heated from the top.*

This is the appropriate mode of firing when the purity and especially the appearance of the acid are of less moment than a saving in fuel and the accomplishment of a large amount of work. The acid in this case is, of course, contaminated by the flue-dust, and is always more or less stained by sooty matters, whence its English name, "brown vitriol," has arisen. These contaminations are quite harmless when it is used for decomposing salt, for superphosphate, and for many other purposes.

On the other hand, the rate of evaporation with a fire from above is very quick, because, first, the hot gas is brought into immediate contact with the acid, and can thus communicate its heat much better to the latter than when the two are separated by metallic plates; secondly, the vapours formed thereby are at once removed by the draught, which, as is well known from experience, very much assists the evaporation. Moreover, fired from the top, the pans, if properly constructed, are much less acted upon than when fired from below; especially the danger of being burnt through from the workmen's carelessness is much diminished.

Concerning the loss of acid in evaporation no experiments have been published; probably it is somewhat larger than with pans heated from below, as the stream of fire-gases, acting upon the boiling acid, carries some of it away in the so-called "vesicular" form, *i. e.* as a mist of minute liquid drops, not in that of vapour, but more difficult to condense than the latter (comp. below).

According to the above, pans with top-heat are especially suitable for alkali- and manure-works or for acid to be sold to the latter, but less so for sale-acid intended for other purposes. These were at one time far more extensively used in England than pans with bottom-heat; but, like them, have mostly become superfluous where Glover towers are employed. Such pans have been described by Godin ('Annales des Mines,' 1865, p. 344) and by myself (Dingl. Journ. cci. p. 352). In any case the lead must be protected from direct contact with the fire, or at least the pans must be cooled in such a manner that the lead cannot melt. The best way of doing this is to keep the pan always filled to the same level, and that near to its top, leaving only a sufficient margin to prevent any boiling-over. In ordinary work the acid is never drawn off altogether unless for repairs; but, the concentrated acid being heavier and sinking down, it is continually drawn off from the bottom, and fresh acid is constantly run in at the top, as long as the concentrating process goes on. Even then the empty portion of the pan has to be protected, especially at the fire-bridge; and, in many English works, for this purpose formerly a lead pipe was burnt on all round, through which ran a continuous stream of cold water. This contrivance cannot be highly recommended, because the pipe soon gets leaky. Moreover the raising of the water costs something; and therefore the following arrangement is preferable.

Fig. 340.

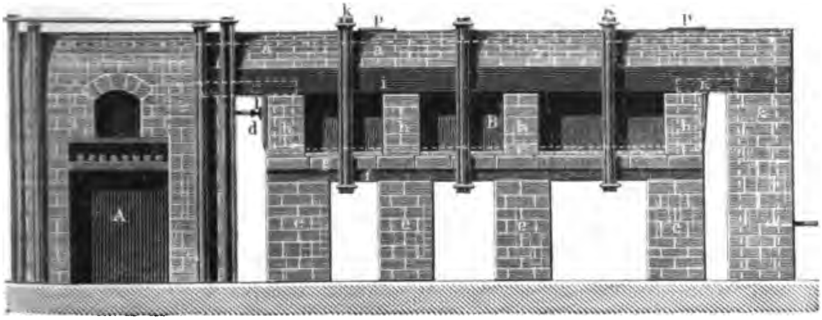


Fig. 341.

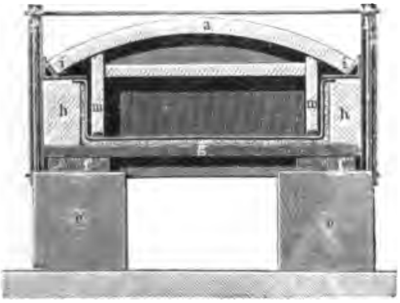
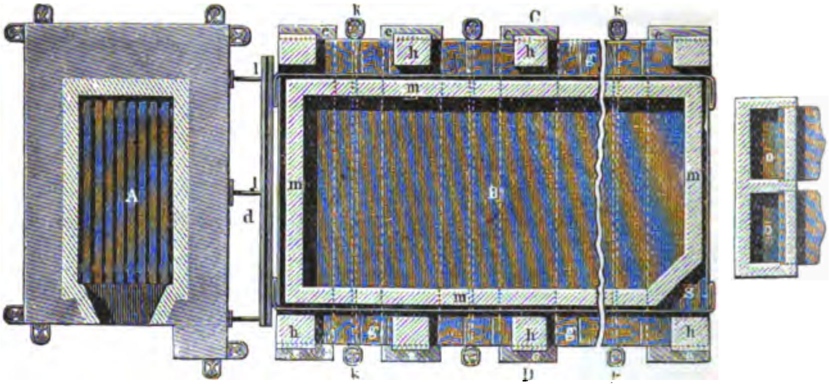


Fig. 340 shows a front elevation, fig. 341 a cross section, and fig. 342 a plan of a pan with top-heat. The fireplace, A (2 ft. × 4 ft.), is built up quite independently; its only connection with the pan B is by the arch *a*, and the fireclay slabs *c*, 2 feet long, lying on the fire-bridge, *b*; the slabs *c* have a 6-inch hold on *b*; and as the space *d* between A and B is 1 foot wide, they project 6 inches into B. The fireplace A is here shown as a plain grate; it might, of course, be more rationally constructed, and at some works it is replaced by a gas-producer. The air-channel, *d*, prevents any injurious effect of the heat of the fireplace on the pan, and we need only regard the flame itself in that respect.

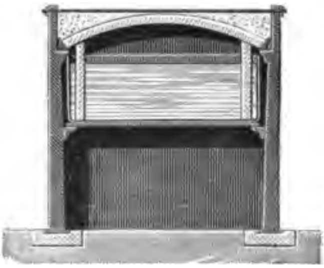
Fig. 342.



The pan B is always made of a single sheet of lead, weighing from 15 to as much as 30 lb. per superficial foot; the corners are not made by cutting out, but by folding over, as shown plainly in fig. 342. Since such stout lead cannot easily be bent cold, along the line marked out for the folding a small fire of shavings is made, of course taking care to avoid melting the lead; the lead then softens sufficiently to be bent with ease. The pan is placed on brick pillars, *e e*, standing quite free, so that the space between them and below the pan is accessible at any time. On the pillars strong wood beams, *f f*, are laid; and across these 3-inch planks are placed close together; they are covered with a thin layer of sand, on which the pan itself is set. The pillars and beams project on each side 10 inches beyond the pan, and thus support small brick pillars, *h h*, 9 inches square, not quite touching the lead, and connected together at the top by cast-iron girders, *i i*. These have an angular section, and serve as springers for the arch *a*, which is thus quite independent of the pan. In themselves the pillars, *h h*, are much too weak to bear the side pressure of the arch; but this is kept up by the binding-rods, *k k*. The upper margin of the lead pan is bent round at a right angle and jammed in between the pillars, *h h*, and the girders, *i i*; in this way the sides of the pan are kept stiff. Next to the fireplace, where the pan becomes hottest and most readily gives way, it may be protected by iron rails and stays, *l l*.

A neater, but rather dearer, plan is this:—Instead of the brick pillars, *e e*, cast-iron columns are provided, carrying, about halfway up, brackets, upon which metal plates for supporting the pan-bottom are laid. The columns are connected at the top by metal girders serving as springers for the pan-arch, and are kept together by bracing-rods. Fig. 343 will make this plainer.

Fig. 343.



The proper protection of the pan from the fire is brought about by the dry wall, *m m*, built up all round within the pan, of the best, hardest acid-proof fire-bricks or stoneware slabs. At the long sides this wall reaches up to the arch; at the fire-end it only reaches to the upper margin of the pan, and there carries the projecting fireclay slabs, *c*; at the chimney-end there are similar slabs, *n*, reaching up to the down-draught, *o*. The wall, *m m*, stands about 1 inch off the pan-sides, and has openings at the bottom, so that the acid can circulate freely. It is evident that the fire can nowhere touch the lead itself; and, moreover, the pan is also protected outside by the cooling action of the air; so that it cannot possibly melt or even soften. If the sides of the pan are to be stayed against bulging out, it should be done by open grids of cast-iron, which do not prevent the lead from being cooled. The greatest danger of giving way is still left at the fire-end, to which, certainly, great attention must be paid. In the arch there are manholes, *p p*, and an inlet-pipe for acid, whilst the strong acid is drawn off by a siphon from the end *s*, left free by the arch; it is still better to attach to the bottom of the pan an overflow-pipe which rises to its top, and whose mouth can easily be narrowed according to requirement. The pan is preserved better if the fresh, cool acid runs in at the part nearest the fire-bridge, whilst the strong acid is taken away at the opposite end of the pan, where it is coolest. It is always too hot to be used directly; and therefore it is run into shallow lead coolers, stayed by iron or wood frames, of which one is being filled whilst the contents of the other are being used. If the acid should not run off sufficiently strong, either the fire is increased or the supply of weak acid is diminished, or both.

The width of the pan is dependent upon that of the sheet-lead; if for the sides about 17 inches each are allowed, about 4 feet 11 inches generally remain. The length is always much more considerable, rarely below 20 feet, but sometimes as much as 33 feet. The longer the pan, the better the fire is utilized. The consumption of fuel is always much less than for pans with bottom-fires; Bode estimates it at from 10 to 12 per cent. of the strong acid, but I can report from a thoroughly trustworthy source that in properly constructed pans of this kind only 2 or 3 parts of coal are required to make 100 parts acid of 142° Tw. from chamber-acid of 110° Tw. The repairs of a properly constructed pan of this kind are much less than those of a pan with bottom-heat (as they always are in analogous cases); and the work done is much larger for an equal area. A pan of 4 feet 11 inches width by 33 feet length was sufficient, in my experience, for boiling down 80 tons of acid of 144° Tw. per week, from chamber-acid of 116°–124° Tw.

These pans were described exactly as above in the first edition of this book (1879), and that description was taken from the works managed by the author as early as 1866; of course they were known previously to that, although I am not aware who first constructed them. But it would appear that the knowledge of this fact has been forgotten, for when the Hasenclever modification of the Deacon process (E. P. 3393, of 1883, described in Vol. III. of this work) was introduced into England, the pans employed in that process for the purpose of re-concentrating the sulphuric acid, diluted in the process of purifying impure hydrochloric acid, were styled "Hasenclever pans," although they are constructed exactly as shown above, with unessential modifications, *e. g.* a cast-iron grid running along the sides of the pans, instead of the pillars *h h*, fig. 342. These "Hasenclever pans" have in the course of years acquired an unenviable notoriety in consequence of the amount of acid carried away into the chimney, probably not at all in the state of vapour, but of a "vesicular" mist produced by the boiling of the acid in a stream of fire-gases. Constant complaints have been made in that direction, and especially the 35th Report on Alkali &c. Works swarms with them. In the 36th Report, however, for the year 1899, p. 18, it is remarked that at one works a very great improvement had been effected, not that the "total acids" were very materially reduced, but that they are discharged in a less vesicular physical condition, so that their density is less and they do not, as is otherwise the case, fall heavily among the neighbouring streets without diffusion and dilution in heavy weather. This improvement has been brought about by firing with gas-producers. The primary air is carefully regulated, and the secondary air is heated up by what would otherwise be lost by radiation. This secondary air is introduced into the (sufficiently large) combustion-chamber at such a point that immediate contact of the flame with heated acid is avoided as much as possible.

According to the 38th Alkali Inspector's Report, p. 75, the firing by means of producer-gas, while keeping the acidity of the escaping gases more constant, had failed to reduce the amount of acidity, as the fire-gases leave the pans at far too high a temperature. The Inspector strongly recommends to abandon the ordinary system of surface-heat evaporation in favour of the Kessler furnaces (comp. below).

Clough ('American Patents, Official Report,' i. p. 495, iii. p. 166) has proposed a similar apparatus for concentrating the acid up to 170° Tw. His pan was protected from the fire, inside by a wall and outside by cold water contained in an iron jacket. This can hardly be put into practice, because the loss of acid vapours would be too great, and the pan would not stand the wear and tear, in spite of the water-jacket.

2. *Lead Pans with bottom-heat.*

These pans are mostly made of much smaller size than those with top-heat; the essential reason of this is the different wear and tear which they suffer according to whether they are more or less exposed to the fire; moreover the concentration in this case is very regular, the pans always being arranged in sets, so that the weak acid flows in at one end of the set and runs over from one pan to another till it runs off sufficiently strong at the other end of the set, in order to be used up or sold, or to be further concentrated in platinum vessels. Sometimes, however, long pans made in one piece are used, especially in England. In that case the first part, nearest the fire, is protected by an arch, the larger part of the pan-bottom behind this by fire-clay slabs or metal plates. Such a pan is shown in our second edition pp. 664 & 665.

The metal plates are sometimes covered by a thin layer of sand, in order to communicate the heat evenly to the pan; but this greatly hinders the heat-convection. The pan is stiffened inside by iron stays covered with lead; and it is covered by an arch to carry off the vapours into the open air or into the chambers—the latter rarely.

On the Continent small pans are very generally used, of 5 to 7 feet length and width, and from 12 to 16 inches depth, of which from four to six form a set. They are made of 15- to 18-lb. lead, mostly by bending up the sides and folding over (not cutting out) the corners. Sometimes such pans, instead of being made of sheet-lead burnt together, are *cast*, about ¾ inch thick. They are in that case exposed to the fire directly, without interposing iron plates. This plan cannot, however, be recommended. Such cast pans, being much thicker, are dearer than those made of sheet-lead; and they are much more liable to have unsound places, which are very soon eaten through. They are often set in steps, each pan about 2½ inches lower than the preceding one; in other cases, however, they are placed with their bottoms at the same level, but are made of different depths—the pan which receives the weak acid being the deepest (16 inches), and each following one a little less, the last pan (for strong acid) being 12 inches deep. In this way the acid can also flow from one end of the set to the other. At the Oker Works there is a long pan divided by partitions into seven compartments of equal height and level; the fire-grate is in the centre of one side; and the flame first passes in the centre to the back, and then returns at both sides to the front of the pan.

The acid is sometimes carried over from one pan into the next by continuously acting cup-siphons. But as such siphons frequently cease to act in consequence of air getting in, owing to the slow current and the small difference of level, an overflow-pipe ought always to be provided to prevent the pans from running over. It is even preferable to replace the siphons altogether by overflow-pipes, which take the acid from the bottom of one pan and allow it to run on to the top of the next one; but this arrangement requires the work of a very good plumber, to last without continual repairs. The chamber-acid is constantly running into the first pan in a regulated stream; and the strong acid runs off from the last pan without any further interference, the supply being so regulated that the proper strength is obtained.

The pan-bottoms are always stayed and protected from the direct action of the fire by cast-iron plates, which are thicker at the fire end than further off—say, decreasing from 2 inches down to $\frac{3}{4}$ inch. Frequently the first pan, below which the fireplace itself is built, is protected by an arch. MacDougall (Engl. pat. 21,778, 1895) employs perforated cast-iron plates for supporting the bottom, preferably in the shape of a grid with longitudinal and transverse rills, leaving diamond-shaped holes. This indeed, according to 'Alkali Report' No. 31, p. 54, prevents a local overheating of the pan-bottoms, which readily occurs with solid cast-iron plates, and the pans do not show any buckling even after prolonged use.

Carulla (Journ. Soc. Chem. Ind. 1893, p. 15) interposes a copper plate $\frac{9}{32}$ in. thick between the lead and the ordinary solid 1-in. cast-iron plate, which, owing to its good conduction of heat, very efficiently prevents local overheating of the lead without interfering with the transmission of the heat.

Opinions differ as to the way in which the firing of the pans should be arranged. Formerly the usual arrangement was that of putting the fireplace under the strong pan, and allowing the fire to travel towards the weak pan, which receives it last of all. In this case the greatest heat exists where it is most required, since the concentration of the strong acid is more difficult and its boiling-point higher, and since the fire-gas eventually comes into contact with cold acid. When the pans are set terrace-fashion, the fire takes its most natural direction, viz. upwards. At the Rhenania Works the pans are still set in this way.

Practice has, however, mostly decided for the opposite plan, namely, arranging the fireplace under the weak pan, so that the strong pan is furthest from the fire. In this case the strong pan, which is otherwise worn out very quickly, suffers hardly more than the others, and the evaporation still goes on at a satisfactory rate, although there may be a little more fuel used than with the old arrangement, which is undoubtedly more rational as an evaporating-plant, but less adapted to the special needs in this case.

Bode cites the temperature and strength of the acid in a set of six pans, where the fire travelled in the same direction as the acid, viz. :—

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.	5th pan.	6th pan.
	°	°	°	°	°	°
a. Temperature 25°......	112	150	160	148	145	143 C.
Strength 110°	113	120	128	134	140	144 Tw.
b. Temperature 24°......	110	145	156	145	142	142 C.
Strength 110°	113	118	126	134	140	144 Tw.

Here the hottest pan is the third; so that the fire is badly utilized. According to his experience this set required 20 parts and upwards of coal to produce 100 parts of acid of 144° Tw.; whilst in the set figured on pp. 821 & 822, where the fire meets the acid, only 15 to 16 parts of coal were used (on the average of several years). For each ton of strong acid, in 24 hours about 20 superficial feet of pan-bottom may be reckoned; the whole set, therefore, furnishes 6½ tons every 24 hours.

Bode gives the temperatures and strengths of the acid during concentration in pans with the old style of setting as follows :—

Set of four pans :

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.
	°	°	°	°
Temperature 20°..................	52	78	120	138 C.
Strength 106°	...	...	...	144 Tw.

Set of three pans heated by the pyrites-burners :

Acid running in (heated previously).	1st pan.	2nd pan.	3rd pan.
	°	°	°
Temperature 70°........	105	128	147 C.
„ 57°.....................	92	106	125 C.
Strength 106°	...	...	144 Tw.

According to Hasenclever, it is well to regulate the working of the pans by thermometers, in order to avoid any risk of damaging them.

Figs. 344 to 347 represent the set of pans designed and constructed by Bode, where the fireplace is outside, in order to save the first pan. From this, by means of a pan-area of 118 superficial feet and a fire-grate of 6½ superficial feet, 5 tons of strong acid could be produced every 24 hours, with a consumption of 12 to 14 per cent. of Silesian coal. Figs. 269 to 272, pp. 669 & 670 of our second edition, show a modification in which a Fairbairn's double fireplace is used. In all of these the strong pan is placed over the fire, as usual formerly, whilst at the present day the order would be reversed.

Fig. 344.

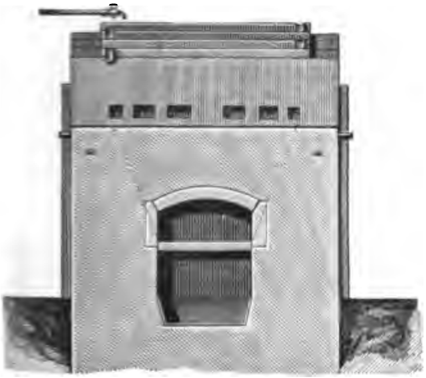


Fig. 345.

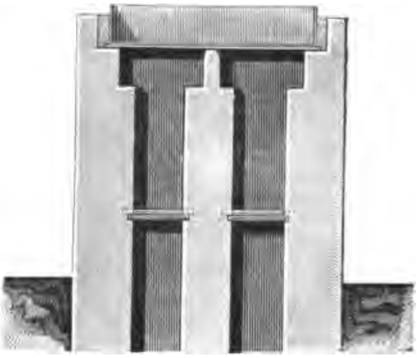
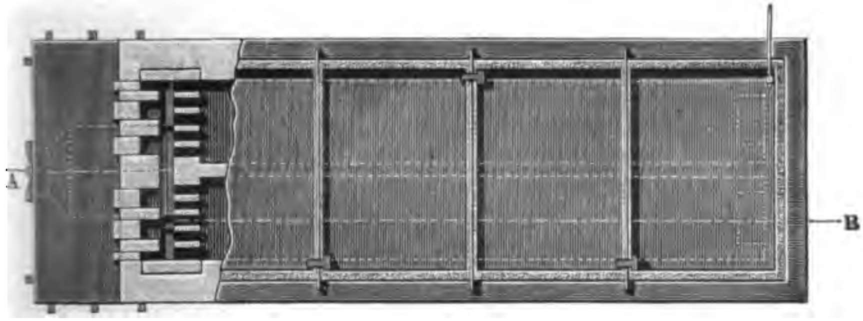


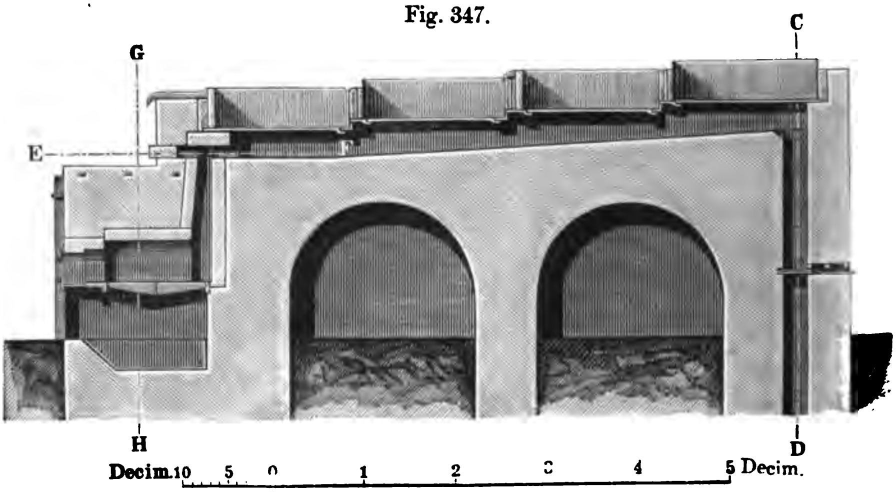
Fig. 346.



According to Scheurer-Kestner (Wurtz, 'Diction. de Chimie,' iii. p. 159), four pans, 6 feet 6½ inches by 3 feet 11 inches each, permit the concentration from 109° to 152° Tw. of sufficient acid to produce 3 tons of concentrated acid daily, with a consumption of no more than half a ton of coals.

Bode calculates the cost of erecting a concentrating-apparatus like that shown in figs. 344 to 347 at £150, and that of keeping it in good working order at 12 per cent. per annum. The cost of the concentration itself, reckoning coals, wages, and wear and tear, in four actual cases, amounted to from 2*s*. 3½*d*. to 2*s*. 8*d*. per ton.

Fig. 347.



Junge (Jahrb. f. Berg- u. Hüttenw. f. Sachsen, 1892; Zsch. angew. Ch. 1893, p. 61) describes the bottom fire-pans as used at Freiberg. They are about 6 ft. 6 in. long, 3ft. 3 in. wide, and 8 in. deep. They are supported by ⅞ in. cast-iron plates and are arranged in tiers, the fireplace being underneath the strong bottom pan and the acid running in at the top pan. These pans furnish a uniformly strong acid, and consume only two-thirds as much fuel as the steam-pans. They suffer, however, under the disadvantage that the first, strong, pan is quickly worn out. [It is strange that Junge does not even mention the arangement, represented as the only rational one on p. 819, in which the fireplace is situated underneath the *weak* pan, in order to lessen the wear and tear.] Sometimes the pan-bottom is suddenly decomposed, the cause of which is unknown. [The explanation of this phenomenon is given by the investigations of Lunge and Schmid, p. 209; or else by the cause mentioned on p. 801.] In normal work the temperature of the acid running off is 200° C. [This is much higher than has been hitherto observed, and this may explain the great wear and tear.]

Very good results have been obtained with a system in which the fireplace is arranged underneath a platinum dish, covered with a water-cooled dome and protected by a brick arch below.

From this the fire passes underneath the lead pans, in which the acid thus never exceeds 160° C. or 58° Bé. The sudden destruction of the first pan never happens in this case. After 15 to 20 weeks' use it begins to leak slightly, so that the acid can be drawn off before any trouble arises. The first pan now lasts 3 or 4 months, the second 2 or 3 years, the others 5 years, and they can be replaced within 12 hours at a trifling cost. This apparatus, inclusive of the platinum dish, costs about as much as the steam-apparatus described p. 828, inclusive of the steam-boiler; it requires much less space, is quite as safe, and furnishes a stronger and more uniform acid, with a much smaller consumption of fuel.

The Zeitzer Eisengiesserei (G. P. 99,768; Fischer's Jahresb. 1898, p. 328) employs a cylinder of antimony-lead, heated inside by fire-gases (?), and fitted on the outside with a number of antimony-lead dishes arranged so that the acid overflows from each dish to the lower one.

Wolters (Engl. pat. 18,831, 1893) carries the evaporation in lead vessels beyond the usual extent, preventing the action of the acid on the lead by saturating the acid with lead sulphate. An excess of this is put in and is kept in suspension by mechanical stirring. Most of the dissolved lead sulphate crystallizes out on cooling and can be used over again.

3. *Lead Pans fired by waste heat.*

In works where there are platinum apparatus for making acid of 170° Tw., the fire of these can never be so far utilized that the waste heat could not be employed for heating lead pans; and this is actually done in most practical cases.

Much more generally applicable, and quantitatively more efficient, is the utilization of the waste heat of pyrites- or sulphur-burners for concentrating chamber-acid. Where there is no Glover tower (which utilizes that waste heat in a different and even more thorough manner) the above process is most rational, since here also the same operation that produces the concentration of the acid fulfils another useful function, that of cooling the burner-gas before it enters the chambers.

The pans used here are generally made exactly like those for concentrating with bottom-fires. They are mostly placed on the pyrites-burners themselves: they must not, however, be set directly upon the burning pyrites, nor even with merely a metal plate between, but must be separated from it by a brick arch. In most cases a gas-flue is placed immediately over the burners, serving at the same time as a dust-chamber, on the top of which the acid-pans are placed (see the diagrams of Malétra burners, pp. 335 & 336). Sometimes, from fear of leakage from the pans into the burners, they are not placed over these, but upon a continuation of the gas-flue. Hasenclever even advises building a second gas-flue, to be used during the time when the pans have to be repaired. The heat of the kiln-gas will not thus be turned to account so well as if the pans stood directly upon the burners; and the danger of leakage into the burners can be avoided by providing the metal plates, on which the pans rest, with a flange all round and an outflow for any acid collecting in it, like those used in nitre-ovens. Leakages occur also less easily where the pans are very shallow, so that the depth of acid is only a few inches. But, on the other hand, it has been noticed that sometimes, especially in the case of poorer ores, the pans on the burners withdraw too much heat from these to be conducive to good burning. For this reason they have been abolished at the Oker Works.

Whilst at some places such pans on the top of the burners concentrate all the chamber-acid from 112° to 114° Tw., at others this cannot be done, and a little extra coal is required for completing the concentratiom.

The diagrams, figs. 348 to 354, represent pans designed by Bode, along with the pyrites-kilns used by him. The apparatus shown here belongs to a set of chambers of 40,000 cubic feet capacity; and each burner receives daily 16 cwt. of Westphalian pyrites containing 42 per cent. of sulphur. The grate of each burner has a surface of 34·4 square feet; the grate-bars are elliptical, 3 inches by 1½ inch, each of them movable; the arch is 4 feet 4 inches above the grate, with a spring of 7 inches. The diagrams show how each burner can be cut off separately. The pans are 6 feet 3 inches by 4 feet 2 inches by 1 foot 2 inches, made of sheet-lead weighing 8½ lb. per superficial foot. They supply daily, when 1½ ton of pyrites is burnt, altogether 2 tons 5 cwt. of acid of 144° Tw. (that is to say, 5 cwt. in excess of the make of the chambers); but as at the same time from 15 to 18 cwt. daily have to be evaporated for the Gay-Lussac tower, the excess causes no inconvenience. Each year three new pans used to be put in, a pan never being left until actually burnt through, but replaced as soon as the lead had become too thin—a plan most decidedly to be recommended in every case. The renewal only refers to the strong-acid pans; those for weak acid are hardly injured at all. The former are therefore much better made of thicker lead, say 30 lb. to the superficial foot, in which case they last for about two years.

Fig. 348.

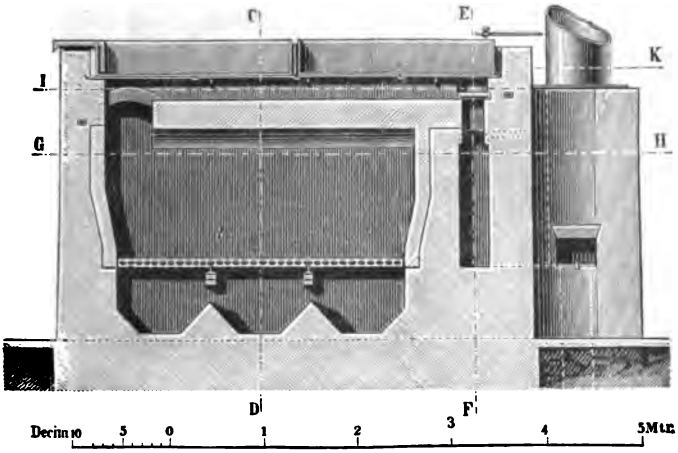
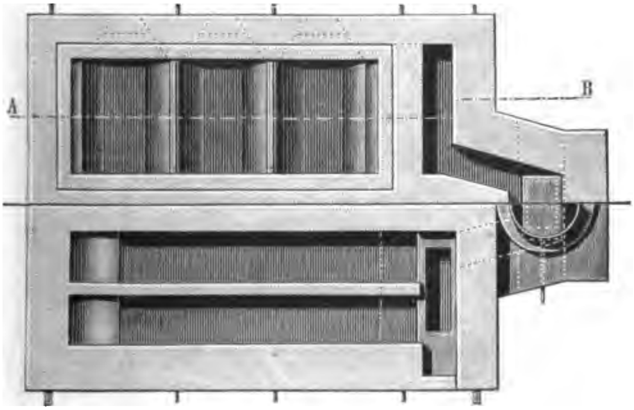


Fig. 349.



The cost of concentration with such pans only amounts to a small fraction of the wages of the burnermen, in addition to the expense of renewing the pans; Bode calculates it, for a special

Fig. 350.

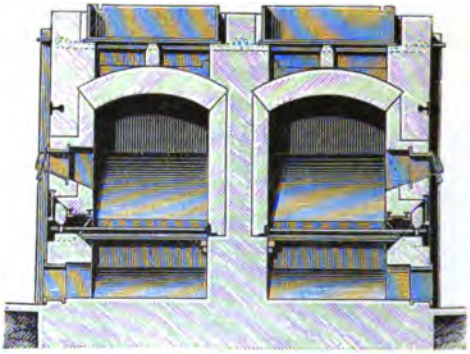


Fig. 351.

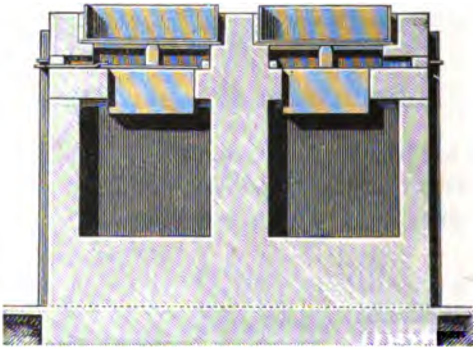
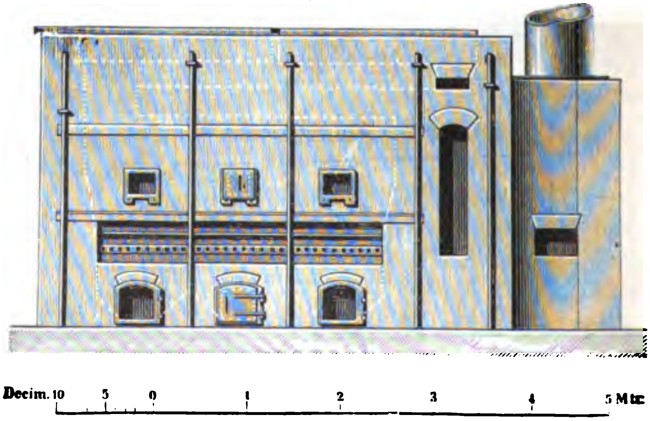


Fig. 352.



case, at 4½*d.* per ton of strong acid; for less-favourable cases he estimates it at 6*d.* to 9*d.* per ton.

Fig. 353.

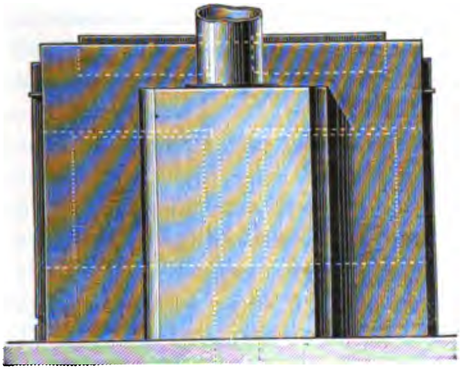
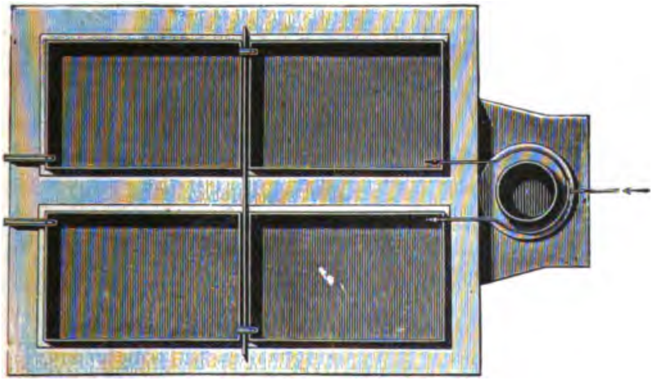


Fig. 354.



Some manufactures and managers still hold that it is irrational to concentrate the acid on the top of the burners, because the trouble and incessant repairs caused by leakages are believed to be far worse than the expense of heating the pans by a separate fire. To this I must oppose that I know of a great number of works where all the pyrites-kilns are provided with pans placed on the top, and where this arrangement has been at work for many years (in a special case I can speak of 30 years) without giving any trouble whatever. This is proof conclusive that the troubles from leakages complained of are caused by a wrong setting of the pans or else by keeping too deep a layer of acid in them (the latter being a very important circumstance). Where they are not placed directly over the kilns, but over the gas-flue (this flue is mostly itself placed on the top of the kilns), and where they are properly protected below by metal plates and a thin sand-bed, they stand as long as may be desired, provided that only a shallow layer of acid is kept in them. Indeed, it may be said that such an arrangement of utilizing part of the heat of the pyrites-kilns, and allowing the other part to act in the Glover tower, is decidedly the best and cheapest plan, where the acid is required of purer quality than can be obtained from the Glover tower; the latter then acts much more as a denitrator than as a concentrator, and the acid produced in it is principally used for the Gay-Lussac tower, the surplus only being used or sold for other purposes.

With *brimstone-burners* it is equally possible and altogether rational to employ their heat for concentrating sulphuric acid. In this case the burners are not covered with an arch, but with 1-inch cast-iron plates, and shallow lead pans are placed immediately above these. Such an arrangement is distinctly shown in Dr. Stahl's sulphur-burners (*suprà*, p. 274); in H. Glover's burner (p. 279) it is combined with a platinum dish. This partial utilization of the heat of the gases does not at all prevent their employment for working a Glover tower. I have seen this combination carried out in several places in America, where the Glover tower denitrates and concentrates all the acid destined for working the Gay-Lussac tower, while the acid for sale is concentrated up to 140° Tw. in lead pans placed on the top of the brimstone-burners. The Glover acid in these cases still issues about 150° Tw. strong, and 126° to 130° C. hot.

4. *Concentrating-pans heated by steam.*

According to Hasenclever (Ber. d. deutsch. chem. Ges. v. p. 504), the idea of concentrating sulphuric acid by means of indirect steam was first proposed by Carlier, the Manager of Messrs. Curtius' chemical works at Duisburg*. After several trials at that works they now use wooden tanks lined with lead, 13 feet square, on the bottom of which lie two lead coils, each of 150 feet length, 1¼ inch bore, and ¼ inch thickness of lead, for conveying steam of 45 lb. pressure. The bottom of the pans is shaped like a truncated pyramid, for the purpose of more easily running off the condensed water; so that the tanks are 2 feet deep in the centre, 1 foot deep at the sides. The two ends of each steam-coil are connected with a lower-placed steam-boiler, into which the condensed water continually flows. When the acid has arrived at 140° Tw., it is run into a leaden tank, through which a lead coil passes; the fresh chamber-acid runs through this coil; and, in cooling, the strong acid gets a preliminary heating. With the above apparatus 5 tons of strong acid can be obtained from chamber-acid of 160° Tw., every 24 hours, by the consumption of 9 cwt. of coals. The steam-boiler requires only as much fresh water as gets lost through leakage at the flanges &c. It is advisable to place a wooden hood over the steam-tank, to prevent any danger from acid being splashed about in case of a steam-pipe bursting. Owing to the low temperature, no acid at all is evaporated; the process is very cleanly, and economical as to consumption of fuel and labour. This Report of Hasenclever is fully borne out by Bode. Hasenclever (Hofmann's Report, 1875, i. p. 185) states the corrosion of lead to be equal to 0·44 lb. of lead per ton of acid. The steam-pipes are mostly acted upon in the places where they dip into the acid, because the dust accumulating there raises by capillarity some acid above the level of the remainder, and this becomes too highly concentrated by evaporation. Since a lead jacket has been burnt to the steam-pipe at the place in question, the above drawback no longer exists.

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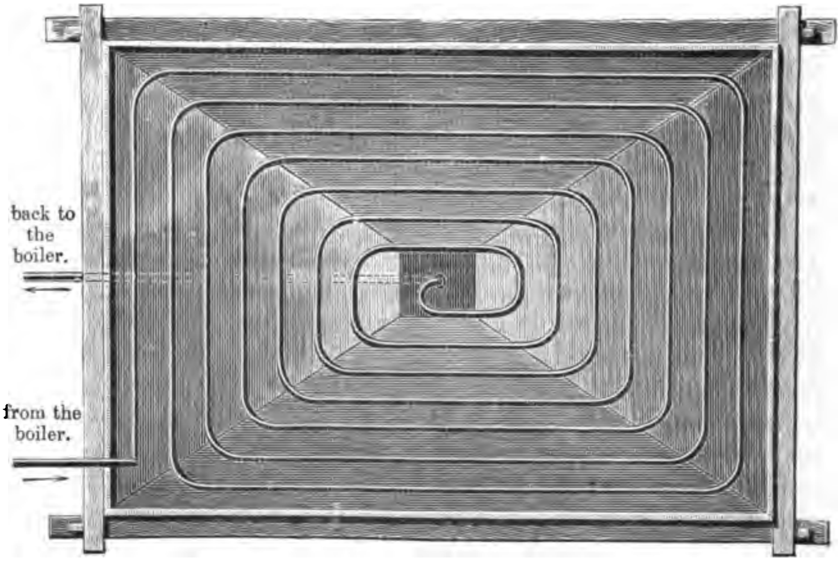
* He seems to have overlooked Smith & Savage's U.S. P. No. 41,647, of 1864.

Figs. 355 & 356 represent a similar apparatus, copied from Bode's 'Gloverthurm,' p. 27. The tank here measures 10 feet 6 inches by 14 feet 9 inches at the surface, 1 foot 4 inches depth in the centre, 1 foot at the sides, is heated by steam of 37 lb. pressure, and supplies in 24 hours 5 tons of acid of 114° Tw. with a consumption of 10 cwt. of Silesian coal. At some works Bode found a consumption of only 8 cwt., at others, however, from 15 to 18 cwt. of coal for the same quantity of acid.

The steam-coil must have a valve both where it enters and where it leaves the pans, which should admit of being closed from a distance in case of the coil bursting. Both the coil and the return-pipe for condensed water (for which a steam-trap should be provided) must be so laid that the water cannot cause a stoppage anywhere. The lining lead weighs from 6½ to 10 lb. per superficial foot. The whole cost of concentration by these pans, including labour, wear and tear of the pan-lead and of the steam-boiler and coils (using 9 cwt. of coals for 5 tons of vitriol), is calculated by Bode at 1*s*. 8*d*. to 1*s*. 10*d*. per ton of strong acid.

Fig. 355.



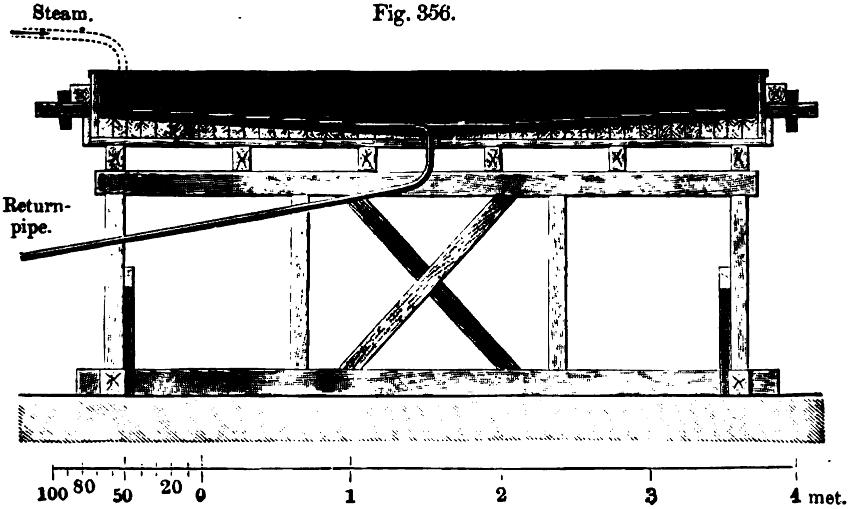
It is very important to place the outlet for acid in such a position that the steam-coil remains completely covered when running off the acid, and is never exposed to the air, which would greatly injure the lead. After a year's work the steam-coil ought to be replaced by a fresh one, even if not showing any outward damage.

Some manufacturers are afraid of running the condensed water back into the boiler, lest the latter should be damaged by any acid getting into it, or even caused to explode; in such cases the above-mentioned larger quantity of coals is used. Bode points out that there is no danger of acid getting into the steam-boiler, because in case of the steam-boiler bursting the steam blowing off will prevent the acid from entering the boiler. The return-pipe must not end below the water-line, but in the steam-dome.

Dr. Stahl recommends employing steam of no more than 30 lb. pressure, in order to reduce the danger of bursting pipes to a minimum.

The process of concentration by steam certainly furnishes the purest acid, and was formerly considered cheaper than the other

Fig. 356.

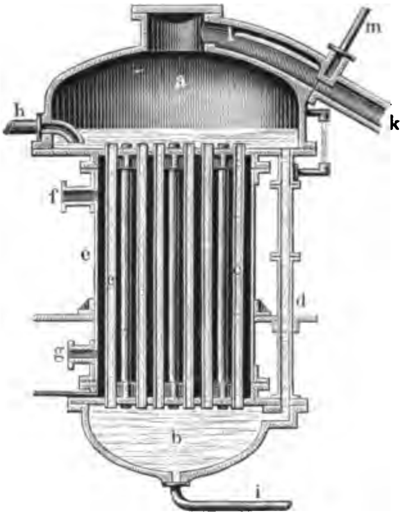


plans, excepting the Glover tower or the pans placed on the pyrites-burners. It has been introduced into several German works, but latterly the reports on the economical working of that plan have not been so favourable as formerly. At Stolberg this plan has been given up again as being too costly.

Several new steam concentrating-apparatus for sulphuric acid have been introduced in connection with ice-making apparatus, all of them founded on the principle of the multi-tubular boiler. We mention of these the apparatus of Kux (G. P. 31,277), fig. 357. The upper part *a* and lower part *b* are connected by many lead pipes, *c c*; through these and the outside pipe *d* the acid circulates. The whole system is surrounded by a shell *e*, into which steam is introduced through *f*, the outlet being at *g*. The thin acid is introduced at *h*, the concentrated acid flows away at *i*; pipe *k* takes away the vapours, and a water-pipe *m* with an inner pipe *l*, perforated by many holes, condenses any acid carried over.

Egells (G. P. 31,620) describes a very similar apparatus, in which the tubes are placed in a horizontal direction, and special precautions are taken against any sagging of the tubes *c*. Kurtz (G. P. 37,713) employs lead pipes provided with inner iron pipes. A combination of a leaden pan with evaporating-worms placed sideways of it forms the subject of a patent of the International Vacuum-Eismaschinenverein (G. P. 38,015; Fischer's Jahresb. 1887, p. 508).

Fig. 357.



Kurtz (G. P. 38,018) describes a steam-heated pan with countercurrent.

Solvay & Co. (G. P. 54,730) promote mechanical circulation in such a pan by a mechanically driven screw-wheel.

Junge (Jahrb. f. Berg- und Hüttenwesen in Sachsen, 1892; Zsch. angew. Ch. 1893, p. 61) describes in detail the steam-heated acid-pans employed at Freiberg. They are flat-bottomed boxes, lined with 5 millim. lead, about 10 ft. × 4 ft. 3 in. and 14 inches deep, with a coil of lead pipe, $1\frac{1}{8}$ in. bore, $\frac{5}{16}$ in. thick, 184 ft. long, resting on loose pieces of lead-piping. Six such pans are combined in a set, communicating by overflows; the acid runs in at one end and out at the other. The steam-pressure is best not exceeding 2½ atmospheres. The temperature rises in the first pan to 125°, and does not go above 128° in the last. The strength of the acid (entering at 51°·4 Bé.) in the six pans is respectively: 53°·9; 56°·1; 57°·4; 58°·6; 59°·4; 50°·2 Bé. Hence a comparatively low pressure, far below the boiling-point of the acid, suffices for concentration; but this involves slower work and much more plant than concentration by direct firing. The cost of repairs is slight so long as the apparatus is new, but subsequently it is very considerable. The thickness of the steam-coils corresponds to a strain of 60 atmospheres in the cold; in spite of this they later on become bulged out and burst with a pressure of only 2½ atmospheres. This is caused partly by the action of steam from within and hot acid from without, partly by the gradual diminution of the tensile strength of the lead used at that high temperature. Lead alloyed with 1½ per cent. antimony (hard lead) cannot be used, as it is quickly destroyed by hot sulphuric acid (comp. p. 209). This occurs chiefly in the places where the hard lead is in contact with soft (pure) lead and galvanic action sets in; but this is noticed only at higher temperatures, not with apparatus worked at the ordinary degree of heat. The steam-pans are gradually very much impaired in their efficiency by lead-mud, &c. settling between the coils; they then furnish less and weaker acid. Hence their use cannot be recommended, except where it is absolutely necessary to avoid any injury to vegetation, which is certainly altogether excluded here, as well as any loss of acid. But they are far more costly, both to erect and to work, than directly fired pans.

Lead vessels for higher concentration than up to 152° Tw. can be used only by the application of a *vacuum* and will be mentioned in a later part of this Chapter.

5. *Concentration to* 144° *Tw. in Platinum Vessels.*

Concentration in platinum dishes, in Faure and Kessler's apparatus.—The inventors state that 7 parts of coal suffice for obtaining 100 parts of acid of 143° Tw. from acid of 106° Tw., of which quantity 4½ to 5 parts of coal may be deducted if the steam be used for the acid-chambers. The same might be done in any other plan; but it rarely is done, because too much air is carried along with the steam. According to Bode, in reality 10½ parts of coal are used, the warm water being utilized for feeding a boiler. This system, applied to concentration up to 144° Tw., does not seem to be able to compete even with the steam-pans, let alone the pans heated by pyrites-burners or the Glover tower, least of all if the cost of plant be considered.

The last Concentration of Sulphuric Acid.

We have seen that we cannot carry on the concentration in lead pans beyond 150° or, at the outside, 152° Tw., the latter not without a somewhat strong action upon the lead. In the Glover tower it is possible to go rather further, as its lead is protected by the lining so as to be acted upon very slightly; the acid does not come into contact with the lead, but only with the flints, bits of pottery, &c., and arrives at the bottom with a temperature of about 130° C.; so that even the bottom of the tower, which is made very strong, is not sensibly acted upon. In fact those manufacturers (being the majority) who work the Glover tower with hot gas from rich ores, and get their chamber-acid up to 120°–124° Tw., regularly attain a concentration of 152° Tw., and in some cases even 156° or 160° is reached. The latter is the exception, and already dangerous to the tower; if it were not so, the concentration by hot kiln-gas in the Glover tower (of course modified to some extent) would be the cheapest plan for the last concentration of the acid, because then the escaping gas goes into the chambers and is not lost at all. We shall see below that this has been indeed attempted.

Concentration beyond the point attainable in lead pans or in the Glover tower is a much more difficult task, involving incomparably more expense than the first concentration. Since the attempts to concentrate the acid up to 170° Tw. by means of cooled lead pans with top-heat (Clough), or by a vacuum (Keller, De Hemptinne), or in towers filled with pebbles and heated directly by heating-gas (Gossage), or other ways had not been successful, and since cast iron is not easily available below the point to which "rectified O.V." is brought in ordinary work, recourse was formerly universally had to apparatus made of glass or platinum, of which the former have the drawback of very restricted size and great liability to breaking, the latter that of being very costly without being proportionately durable. These circumstances make their application both expensive and troublesome.

By far the largest quantity of acid is used of no higher strength than is attainable in lead, mostly even rather weaker. For making sulphate of soda, the acid is never taken stronger than 144° Tw., generally only 140° Tw. The English manufacturers as a rule dilute their Glover-tower acid down to this point with chamber-acid; or they only make as much acid of 152° in the Glover tower as is required for working it, and they keep the remaining acid weaker by running more chamber-acid through the tower. For the manufacture of superphosphate the acid is mostly employed even in a weaker state; and this, along with the sulphate of soda, swallows up most of the total quantity of sulphuric acid made. In the great majority of cases sulphate-of-soda and superphosphate works make their own sulphuric acid, and, of course, do not concentrate it beyond their own requirements.

Touching the acid made for sale, however, a circumstance has to be considered here which in many cases induces the manufacturer to incur the great expense and trouble of concentrating the acid as highly as possible, even in cases where the consumer, not requiring it of such strength, must himself dilute before using it. This is the greater expense of packages and transit for the same weight of real acid in the dilute as compared with the concentrated state. Apart from those cases in which completely concentrated acid is asked for on account of the smaller cost of packages and of transit, or from old habit and ignorance, there are many cases in which the consumer is really obliged to employ an acid of the highest possible strength:—for instance, the purification of rape-oil; that of benzol, paraffin, and other mineral oils; the refining of gold and silver; the production of nitro-cellulose, nitro-glycerine, nitro-benzene, and other nitro-compounds; that of sulphonic acids, for instance those of benzene and anthraquinone for the manufacture of resorcine and alizarine; for dissolving indigo, and many other purposes. In many cases an acid containing from 93 to 94 per cent. of SO_4H_2 will do; and often that which is sold as acid of 170° Tw. does not contain any more, and, if pure, really ought to show only 166° Tw. (=1·83 sp. gr.)*. For making nitro-compounds especially, however, an acid of greater strength is required, containing 97 or 98 per cent. of SO_4H_2; even this cannot show more than 1·840 sp. gr. at 0°, or 168° by a really true hydrometer, unless it is very impure and contains much foreign matters.

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* Recently more correct hydrometers have been used, and the quotations are no longer made for acid of 170° Tw. (which does not exist in the pure state), but 168° Tw.

This "extra-concentrated" acid can also be made in platinum vessels, but at the cost of dissolving much more platinum than ordinary rectified oil of vitriol. In this way it is possible to get up to 98 per cent., or at most 98·5 per cent. These high strengths, as we shall see below, can also be made in cast-iron vessels, which are not suitable for concentrating acids below 96 per cent. For some purposes an acid of as nearly as possible 100 per cent., that is, monohydrated sulphuric acid, is required. This can be made by adding some fuming oil of vitriol to ordinary sulphuric acid; but it can also be made by freezing, as we shall see *infrà*.

Manufacture of ordinary Rectified Oil of Vitriol.

It has already been mentioned that usually either *glass* or *platinum* vessels are used for the last concentration of sulphuric acid. Which of these two materials is to be preferred to the other has been a matter in dispute for a long time; nor is it settled yet, both systems being largely employed. Formerly, before the platinum industry was developed, *glass retorts* were the only available apparatus, and those could only be had of comparatively small size and bad quality. They were also mostly set in "galley-furnaces," a double long row of retorts being heated by a fireplace at one end; thus the retorts near the fire were, of course, much more heated than those more distant, and were much sooner finished, or even overheated before the distant retorts had been sufficiently fired. Each retort was either put into a metal pot, with some sand between, or protected from the direct flame by a covering of clay and horse-dung. Both owing to the inferior quality of the retorts and the unsuitable setting, there was always much breakage, combined not only with the loss of acid, but also with the sudden evolution of suffocating vapours. The cracking of the retorts was especially induced by a cold draught getting at them; and since in that case the workmen had to save themselves instantly from the vapours by leaving the room, frequently the cracking extended to all the retorts. Besides, the expenditure of time, wages, and fuel in this process was very great.

There was always, therefore, an inducement to discover some other material than glass; and the only practicable metal, *platinum*, was at once applied, in spite of its high price and difficult management, as soon as Wollaston's process of welding spongy platinum into ingots and plates was made known. The first platinum still appears to have been made in 1809 in London; it weighed 423 ounces ('Chem. News,' xxxviii. p. 43). Later on platinum stills weighing from 66 lb. to a cwt. were made, holding 4 to 6 tons of vitriol, and costing from £1600 to £2000. This large sum did not deter manufacturers from using platinum for the last concentration of sulphuric acid, because they convinced themselves at once of the large amount, facility, and safety of the work of concentration that could be carried on in them, and because they thought (although erroneously) they could reckon upon such apparatus lasting almost for ever.

The platinum vessels made by Wollaston's process were often porous and unsound, so that acid oozed through; besides, blisters and rents frequently appeared in them, which had to be soldered up with gold. The platinum stills themselves, therefore, gave much dissatisfaction. This, however, has been greatly diminished since Ste.-Claire Deville taught the melting of platinum in large masses by an oxygen-gas blowpipe in furnaces made of quicklime, casting perfectly sound ingots of it weighing 2 cwt., and, further, to solder the joints with platinum itself instead of gold, analogous to the burning of the lead chambers. In London this process was first applied in 1860. Since then the stills have been much more durable and at the same time cheaper, although the unavoidable concentration of the platinum-industry in very few hands still tends to keep the price of platinum apparatus at a very high figure.

When, however, attention was drawn to the fact that platinum itself is gradually acted upon by sulphuric acid (see below), and that thus the large capital expended on the stills not only involved heavy permanent charges for interest, but would have to be gradually written off altogether, and when, on the other hand, great improvements were effected in the manufacture and treatment of glass retorts, the latter came to the fore again, and began to drive platinum vessels out of the field, more especially in England. In 1862 Hofmann mentioned, in the 'Report of the Jury,' that in Lancashire the use of platinum retorts had almost ceased; at that time about $\frac{7}{10}$ of all the vitriol in England was concentrated in glass. In France and Belgium glass retorts existed along with platinum; but the latter held a wider ground; and in Germany it was almost exclusively used. In 1868, the 'Official Report of the International Jury,' vii. p. 34, stated that concentration in glass was then very rare (in France).

In order to meet the competition of glass, the platinum-works made efforts to construct the stills more durable and more cheaply; and they have indeed recovered a portion of the field previously lost. Later on they were urged to renewed efforts in this line by the combination of platinum and lead employed by Faure and Kessler, which has again receded into the background; and eventually the introduction of gold-lined platinum has greatly advanced the use of these vessels.

At the present time the matter stands thus:—Both glass retorts and platinum stills are in use, some of the latter made according to the old and others according to the new system. The glass retorts are mostly used for the rather less concentrated acid, containing 92 to 93 per cent., the platinum stills for the more concentrated acid, 93 to 96 per cent.; in a few cases both are employed at the same works for these different objects. The glass retorts, however, are almost entirely confined to England, and in Lancashire are almost exclusively used; on the Continent, platinum or platinum-gold vessels are used nearly everywhere but in a few places exceptionally well situated for obtaining glass retorts—for instance, Montpellier, where, according to Payen, a retort of 18 gallons capacity only cost 1·6 franc, whilst at Paris and most other industrial centres the price is 6 francs. Since such a retort holds a little over 1½ cwt. of strong acid, and on an average can be used five times, furnishing altogether 8 cwt. of vitriol, the retorts for 1 ton of acid at Montpellier cost 6 francs, at Paris &c. 15 francs. In America both glass and platinum apparatus are used.

If the enormous rise in the value of platinum which has taken place since 1890 should prove to be permanent, the use of glass retorts, and also those of porcelain, cast iron, and the concentration by hot air &c. (see below), will receive a fresh stimulus.

Concentration in Glass Retorts.

The shape of glass retorts now in use for concentrating oil of

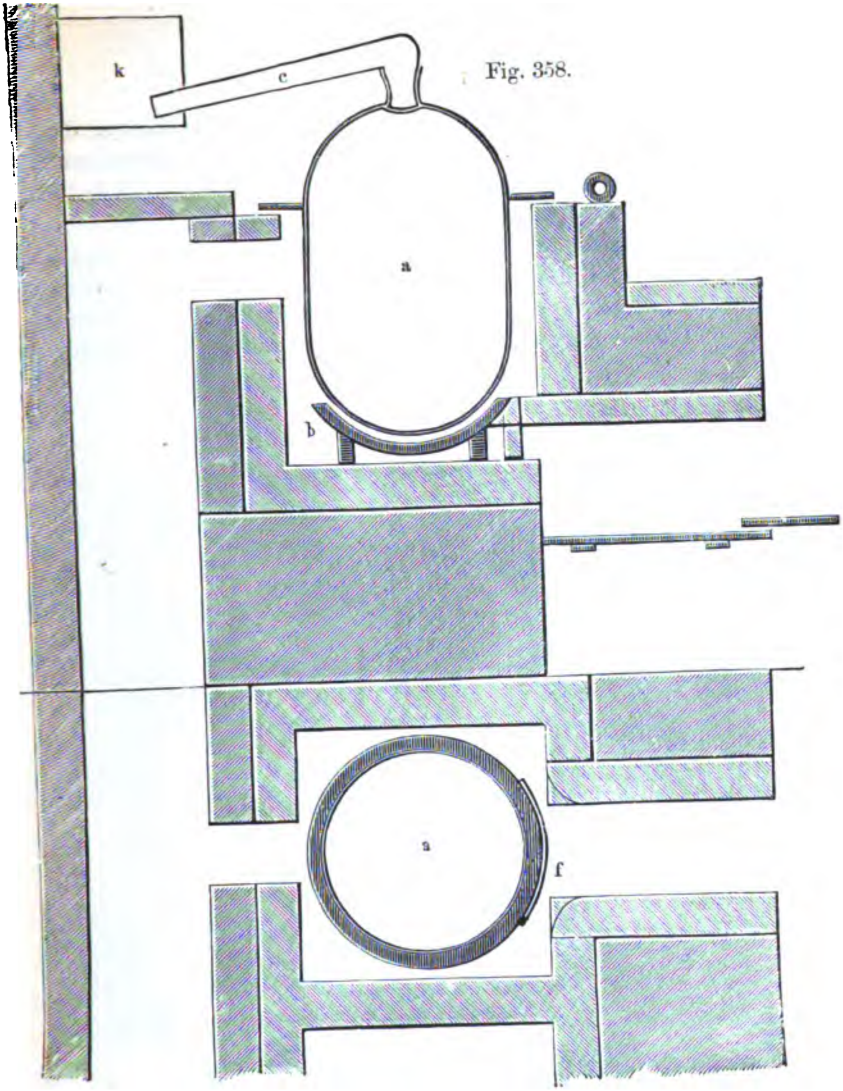


Fig. 358.

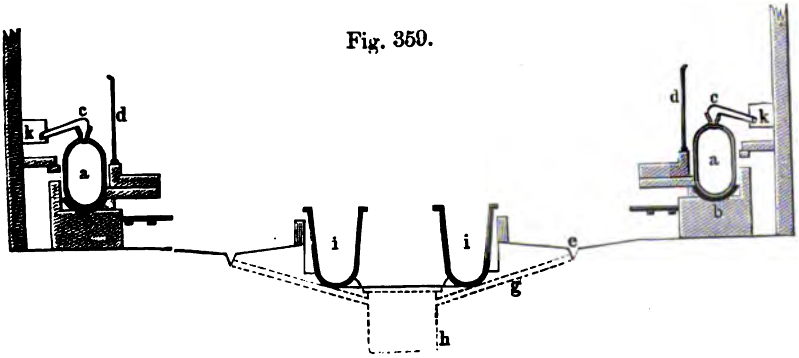
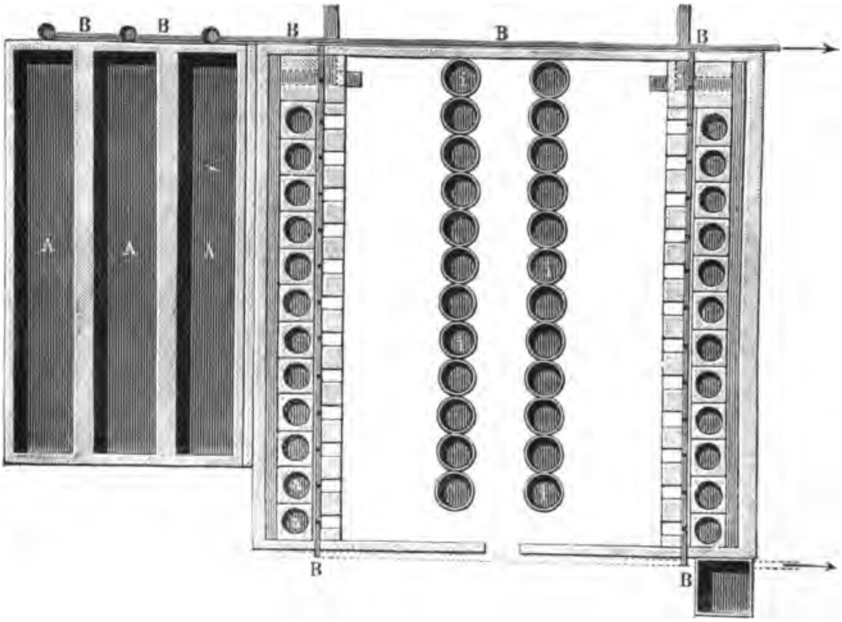


Fig. 350.

vitriol was introduced by Chance Brothers, of Oldbury, near Birmingham, who make them at their glass-works at Smethwick. They are shown in fig. 358 (this, together with figs. 359 & 360, is taken from Roscoe & Schorlemmer's 'Chemistry'). These retorts consist of two separate parts, viz. a large bottle *a*, with a neck at the top, into which fits a loose head *c*, whose other end enters an aperture in a lead pipe or tunnel *k* running all along the retort-house, and ultimately connected with a chimney. The bottles *a* are blown of thin glass, as evenly as possible, about 3 feet high from the bottom to the top of the neck and 1 foot 9 inches diameter. They rest on a flat metal sand-bath *b*, and are protected from direct contact with the flame by the round fire-clay slab *f*. In the pipe *k*, which conveys the condensed acid vapours to a collecting-tank, there is always some suction produced by the chimney draught at the other end; therefore the head *c* needs no cement to connect it with the bottle, as no vapours can get out, only air being able to enter. This is very important, as the head *c*

Fig. 360.



has to be taken off and put on every day. The above-mentioned suction has also this effect, that retorts may be at work with cracks in their upper parts, provided such cracks do not reach down to the level of the acid in the bottle.

Fig. 361.

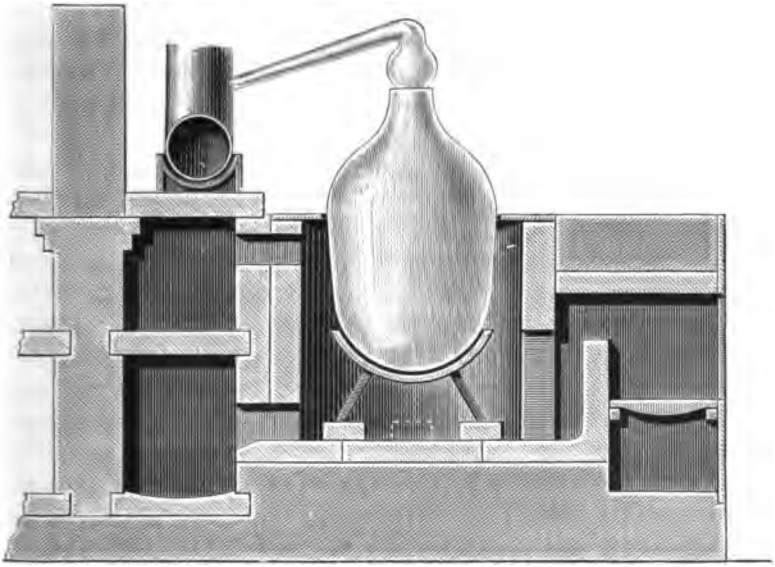
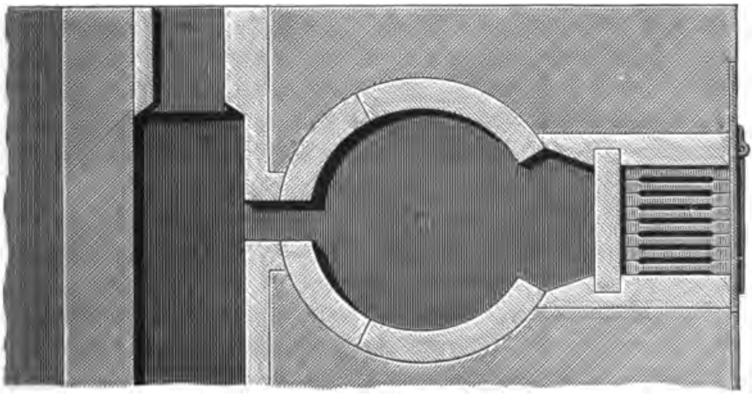


Fig. 362.



A number of retorts are always grouped together, as seen in fig. 360, where A A A are boiling-down pans, from which the main pipe B takes away the hot acid of 144° Tw. On this pipe are fixed long thin lead pipes *d d* (fig. 359), which are bent down at will, in order to fill the single retorts. *i i* are cooling-pots for the strong acid drawn off, from which the carboys are filled. The floor is made a little sloping, so that in the case of a retort breaking the acid runs into the gutter *e*, and from this through pipe *g* into cistern *h*.

An accurate plan (to scale) of a retort-setting is given in figs. 361 & 362; this will be intelligible without further explanation.

The retorts (in number from 20 to 50) are placed in a separate house, the temperature of which is kept constantly at from 25° to 30° C., it being provided with tight-fitting windows and double doors; only one door is opened at a time, the other being shut, so that no draught (the chief cause of the bottles cracking) can enter. A retort-house with 24 retorts can turn out about 5 tons per diem.

The work is carried on in this way:—The distillation goes on all day long, and is finished in the evening. During the night the acid cools down to some extent; in the morning the retort-heads are taken off and the acid is drawn off by siphons of platinum or thin lead tubing with a very narrow orifice. The siphon is filled with cold acid, the narrow opening closed with the finger; the siphon is then put in quickly, and the finger at once washed with water. Sometimes the acid is thus drawn directly into glass carboys, but it is better to employ a series of cooling pots, as shown in figs. 359 & 360. A small portion of the acid is necessarily left in the retorts, and this is useful in refilling them with warm acid of 144° Tw., as it prevents cracking.

In order to prevent the cracking of the retorts by sudden draughts, Jones patented, in 1845, so-called "protectors," consisting of hoods of sheet-iron or stoneware, made in two parts, quite covering the neck of the retort. But as this also prevents observation of the liquid, they are inconvenient; and they are quite unnecessary if the house is arranged as described above—that is to say, if it is kept warm, and draughts are excluded by double doors.

The sulphuric-acid vapours formed in the rectifying process in glass retorts should in no case be allowed to get into the chimney. They are partly condensed in the conducting-pipe itself; after issuing from this, they should pass through a small coke condenser, flushed with water, before entering the chimney, to wash out all the acid. The 21st Alkali Report, p. 45, describes the following arrangement :—The necks of the retorts pass into a lead trunk, set on a level, whose bottom is dished with an upstand of three inches, not burnt to the sides. A small stream of water is set running, when the glasses start boiling, at the end of the trunk nearest the condenser, and the water travels in a contrary direction to the vapours; at the further end it runs out at a lip as acid of 100° Tw. This plan is very effective, and only a small scrubber is required to arrest all the fog of acid vapour escaping from the trunk.

Fehrmann (Fischer's Jahresb. 1886, p. 263) describes the glass concentrating-plant at Mülheim on the Rhine. The retorts have a similar shape to those used in England; they are made at Glasgow and cost at Mülheim about 38*s*. each. There are 32 in a row, holding 6 cwt. each. Each retort is placed in an iron sand-bath to within 4 inches of the neck, and is heated by a separate fire ; a 6-inch sheet-iron partition prevents any splashing over from the neighbouring retorts in cases of cracking. Before putting the arm (head) on to the neck of the retort 3 or 4 small leaden washers are put in which prevent the contact between glass and glass. The charging takes place by means of a leaden main, connected with a higher pan, in which chamber-acid is concentrated to 142° Tw.; from this main a thin lead tube branches off in front of each retort, which is lowered for the purpose of charging. The charging takes half an hour for 32 retorts. The emptying is effected by means of glass siphons, set going by an air-pump. The vapours formed during the process are carried away by an 8-inch pipe running along the retorts; this is connected with large lead cylinders, filled with coke and cooled from without, where the distilling acid is condensed, and from these a connection is made to a chimney. All the fireplaces are accessible from the outside of the building; in front of each retort there is a small glass window which allows of observing the boiling, and thereby regulating the fire. It takes 1 or 2 hours before the acid begins to boil, and the whole concentration lasts 8 to 10 hours; the sign of the end is when the acid has been completely decolourized.

The construction and working of the plant at the Mülheim works have been very minutely described by Lüty (Zsch. f. angew. Chem. 1892, p. 385). This communication would be very important and interesting if the intermittent plan were not now universally recognized as far too expensive, and therefore antiquated; I must therefore refer those still interested in it to the original or to the translation in Journ. Soc. Chem. Ind. 1893, p. 153. The plant described by Lüty (erected by an English chemist) seems to have been even less economical than some others, and is a warning example against the whole system.

In England formerly all sulphuric-acid retorts were made of flint glass, containing upwards of 40 per cent. lead oxide, because this was supposed to stand better, which may possibly have been caused merely by the fact that the retorts were not made to do so much work as in recent times. On the Continent such retorts were always made of ordinary soda-lime glass (crown glass), and this seems to be used in England as well now.

A great improvement on the old plan of intermittent concentration in glass retorts is the *continuously acting plan* of Gridley, patented as a communication by Mr. Henry Chance (No. 1243, 1871). Several retorts are placed terrace-wise in an obliquely ascending furnace and are connected by siphons, so that the top retort is fed by fresh acid, which, after being concentrated to some extent, flows into the next lower retort, and so on. The lowest retort is in the hottest part of the furnace. A retort is shown in detail in fig. 363. *a* is the head, connected with a draught-pipe common to all the retorts, by which the vapours are conveyed into a small leaden coke-tower and condensed by water. At *b* there is an opening in the shoulder of the retort; into this the funnel passes by which the acid enters the retort; *d* shows the level of the acid; *e* is the tubule attached to the retort, by which the acid leaves it; and *ff* show the glass connectors which convey the acid from one retort to another. The retorts are set in sand in shallow iron pots, *g*. Four beds of retorts, *i. e.* sixteen retorts, will produce, from 6 A.M. on Monday till 12 noon on Saturday, 600 carboys, equal to 46 tons; the labour required consists of two retort-men (day and night turns) and two labourers. The average consumption of coal is 28 lb. per carboy

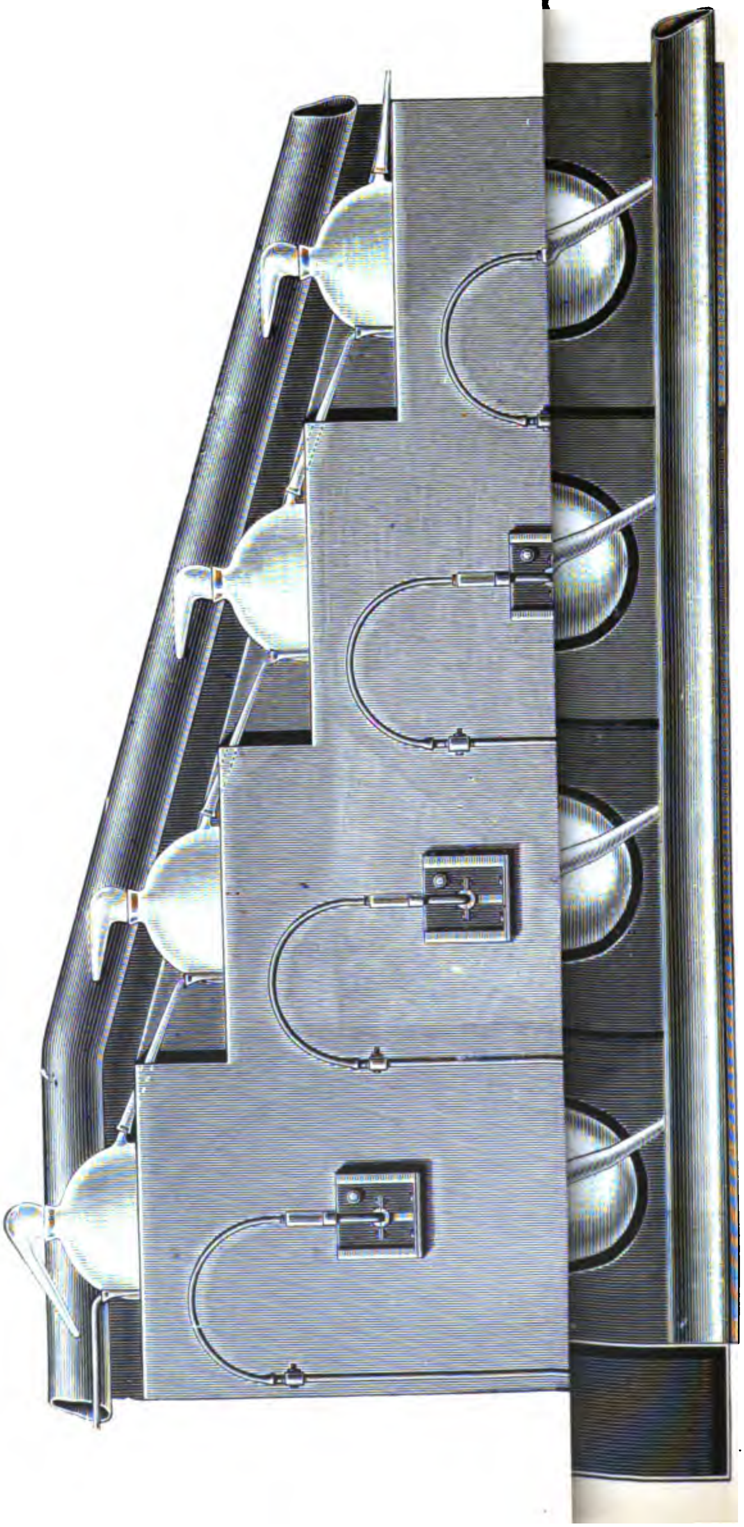
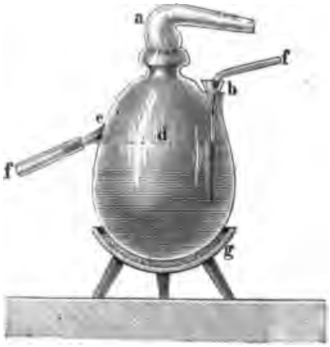


Fig. 364.

of 175 lb. (=16 per cent.). This process is in very successful operation in several vitriol-works in the United States, and has also been adopted by some manufacturers in England.

Fig. 363.



I owe some important communications concerning improvements in the Gridley process to the kindness of Messrs. Chance Brothers, of the Oldbury chemical works, and of their manager, Mr. H. C. D. France. (Part of the following is taken from Dr. Ballard's Report, pp. 173 & 182.) The process has been improved at the above-mentioned works by using ordinary coal-gas as a heating agent, burnt in a Bunsen burner underneath each retort. This has largely increased the output and decreased the labour and breakage. The breakage during a period of two years has only cost 3*d.* per ton of acid rectified, and the labour has been 1*s.* 10*d.*; but this item could easily be lessened, as the same men could look after plant turning out twice as much. The gas consumed (made at the works themselves), with all leakages and defects, has been 3500 cubic feet per ton of acid of sp. gr. 1·84. (The present consumption of gas is probably even less than that here stated.)

Figs. 364 to 366 show the way in which the four retorts are combined in a set, which is fired from a common gas-pipe.

The retorts are first fired till all the acid in each of them has attained full strength; then fresh acid of 144° Tw. is run into the top retort, whereupon the connecting overflow-pipes begin to work and the acid runs from each retort into the next lower one, and from the lowest into a cooler, from which it can be filled into carboys. This process goes on day and night.

A great advantage of the Gridley-Chance plan is this, that it requires no retort-house kept at the temperature of a Turkish bath, like the old plan. It is only necessary to enclose the four retorts themselves in a glass case, similar to the vapour hoods to be found in every large chemical laboratory, in order to protect the retorts against draughts. The glass case is connected by a pipe with a small leaden coke-tower, which communicates with the chimney; any acid vapours escaping from the retorts are condensed here.

The Gridley plant, as arranged at Chance Brothers, is so efficient that with ordinary care breakages of retorts hardly ever occur. But in order to provide against this contigency, the bottom of each fireplace communicates by a pipe with an underground tank; in case of a retort breaking the acid would flow into this tank.

The strength of acid attainable by this (or any similar continuous) process does not exceed 92, or at most 93 per cent., which must not be overlooked in comparing the cost of concentration with different kinds of apparatus.

The cooler for this process is constructed in such a manner that the hot acid first flows through a platinum tube, in which it already loses a good deal of its heat, and then into a leaden box with double walls and external and internal water-cooling. The acid issues perfectly limpid, about 60° C. warm and 168° Tw. strong. (Of course any of the cooling-apparatus connected with platinum stills, as described further on, might be employed here.)

An apparatus altogether similar to Gridley's, in which, however, the glass bottles are replaced by porcelain dishes with glass heads, has been patented by J. Hughes (Amer. pat. 339,552). Bowen (E. P. 2035, 1883) has patented an apparatus on the same principle, with the addition that the vapours from each lower retort pass into the next higher one, so that very little sulphuric-acid vapour leaves the last retort. [Rational as this seems at the first glance, it is still very doubtful whether in this way the concentration will not be interfered with too much.]

Veitch (E. P. 7901, 1889) employs flat-bottomed retorts, arranged one above another on a stepped terrace within a tapering fire-flue common to them all, the fire being placed at the lowest and widest end, and the flue narrowing upwards. The acid passes in a constant stream, travelling through the whole series. All the retorts can be easily seen.

Penniman (Amer. pat. 469,439) employs in a set of retorts arranged stepwise a current of air, which keeps the acid continually agitated, and so prevents their breaking.

Retorts having the lower half composed of glass and the hood of any suitable material are described by Schofield (Engl. pat. 19,780, 1891).

As to the cost of concentrating in glass, the labour is, of course, greater than in platinum stills, and it is also of a disagreeable kind. The consumption of fuel is sometimes absurdly stated to amount to eight times the consumption with platinum stills; in direct contrast is the following statement by P. W. Hofmann, referring to the cost of concentration at Dienze, where 2½ tons of concentrated acid were daily made in glass retorts, viz. for 1 ton :—

	s.	*d.*
4 cwt. of coals	4	0
Wages	3	0
Breakage of carboys	1	0
	8	0

If the precaution be taken of replacing all the carboys by new ones after the lapse of six weeks, whether they seem damaged or not, there is next to no breakage, and the cost of concentration is reduced to 7*s.* 6*d.* per ton (Hofmann's Official Report, 1875, vol. i. p. 188). With this should be compared the very much higher cost for wear and tear of the platinum stills (to be given below), and, on the other hand, the much higher statement by Payen concerning the breakage, which, however, refers to the imperfect retorts of former times. Payen states that at Tennant's works at Glasgow only seven retorts, on an average, break per annum. These retorts are made (by Perceval, Vickers, and Co., of Manchester) from green soda-glass, as even in thickness as possible, blown with special care, and cooled very slowly ; their weight is about 60 lb. each, and they cost 1*s.* 4*d.* per lb.

Another statement concerning the cost of concentrating in glass retorts is made in the 'Mineral Resources of the United States' for 1886, p. 673, as emanating from a large English works where acid of 60° Baumé, coming from the Glover tower [?], is concentrated to 66° Baumé (8 tons per day) :—

	£	*s.*	*d.*
1 ton of coal	0	16	0
Wages and Superintendence	2	0	0
Breakage of retorts	0	8	0
Wear and tear of other materials and interest on plant (estimated to cost £200, at 50 per cent. per annum)	0	6	0
Cost of concentrating 8 tons	3	10	0
Cost of concentrating 1 ton		8	9

[This estimate is evidently utterly unreliable. The amount of coal is absurdly low, the breakage of retorts excessively high. We refrain from quoting the comparative cost of concentration in a Faure and Kessler still given in the same place, as equally misleading.]

The cost of concentrating in a Gridley's apparatus is, of course, considerably lower than in ordinary retorts, as there is less consumption of fuel, less labour, and next to no breakage of retorts.

According to a very interesting comparative survey by Tate (Journ. Soc. Chem. Ind. 1894, p. 208), to which we shall have again to refer, the cost of a battery of glass retorts on the old system, for making 10 tons in 24 hours, ranges from £800 to £1000, inclusive of condensing-apparatus. The cost of concentrating from spec. grav. 1·76 to 1·838 varies very much; but the fuel averages 13 to 14 cwt. and the wages 4*s*. 6*d*. per ton of strong acid. The breakage varies extremely at different places. With the Gridley-Chance system the cost of two sets of four retorts each, for making 23 to 25 tons acid per week, is £200, and £100 for the building. The cost of labour is only from 2*s*. and 3*s*. per ton of strong acid; of coal only two-thirds of the quantity required by the old system is necessary, say 10 to 12 cwt. per ton. [This does not agree with the above statement, and later on only 5 cwt. is spoken of.] The breakage is only about one retort to 180 or 200 tons of acid, or say, 1*s*. per ton (a retort costs 25*s*.; in discussing the paper it was mentioned that the breakage is frequently much higher). Extra-concentrated acid is more easily made in glass than in platinum retorts. Acid contaminated by suspended or dissolved impurities is not easily concentrated by this system, as it causes much breakage.

Concentration in Porcelain Dishes or Beakers.

Messieurs Ch. Négrier et Cie., at Périgueux, have constructed a furnace for evaporating sulphuric acid from 50° to 65½° B. (say, from 106° to 167° Tw.) in porcelain capsules (E. P. 14,022, of 1890) *.

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* This plan has been forestalled by an American patent of W. H. Adams, in 1887 (Scheurer-Kestner, Bull. Soc. Ind. Mulhouse, 1892, p. 317).

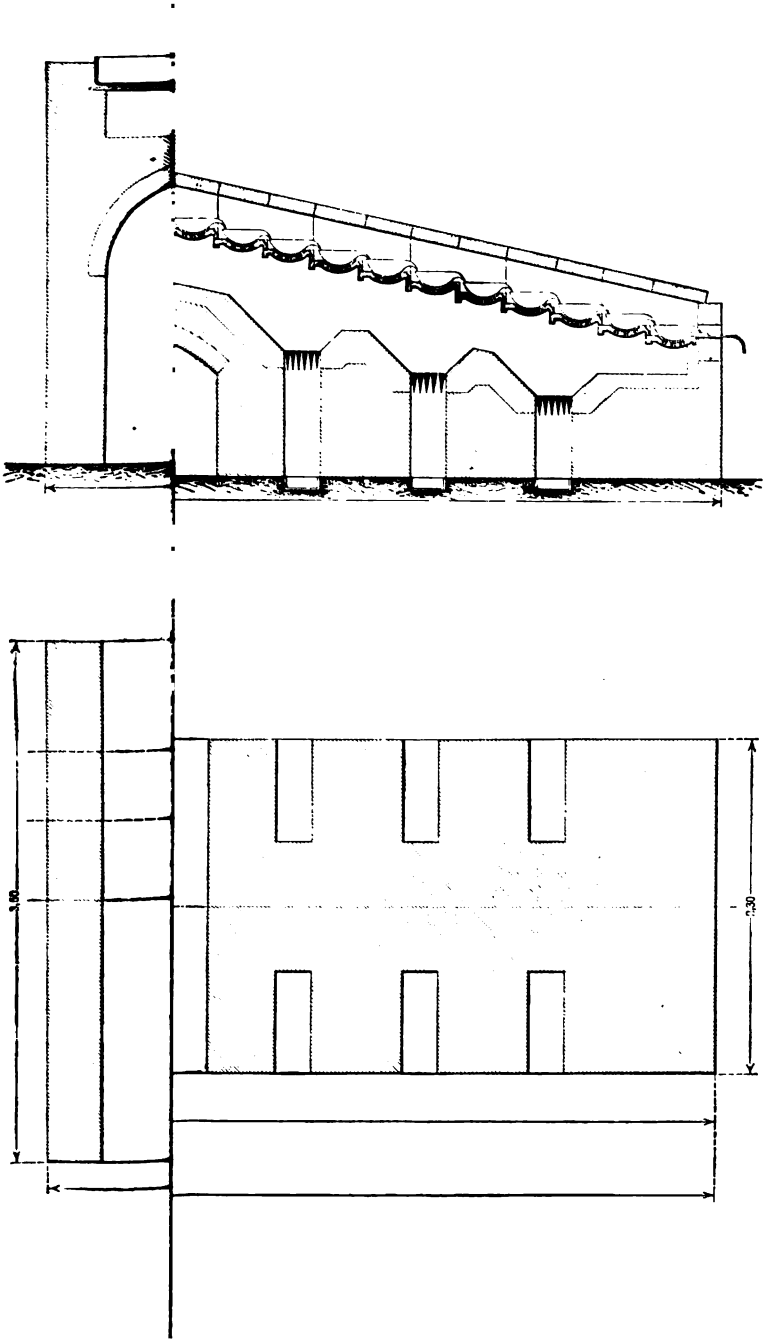
Their apparatus is shown in fig. 292, facing page 693 of our second edition. (It is omitted here as being superseded by Benker's pans, to be shown later on.) It consists of two parallel ranges of 8 porcelain capsules, each placed one above the other, so that the acid overflowing from the lip of each upper pan flows into the lower one. The capsules are semicircular, 0·305 metre wide and 0·135 metre deep. Each two dishes placed on the same level are contained in suitable pans, forming cavities of a single cast-iron plate, reaching from one side of the furnace to the other. Asbestos tissue is interposed between the capsules and the metal pans, in order to protect the capsules and prevent bumping, which is further lessened by putting fragments of porcelain inside the capsules. In the case of a capsule breaking (which happens but rarely) its contents can escape into the fireplace through several holes left in the metal pans; when this is perceived the feed of acid is stopped, the cover is lifted, and the broken dish is replaced by a fresh one in ten minutes. An iron plate with its two dishes lasts three or four years. They are shaped in such a manner that there is no communication between the space below, destined for the fire-gases, and the space above, where the acid vapours are formed, the joints being made good with a cement of asbestos and silicate of soda. When the capsules have been placed in the pans, a layer of coarse sand is put into the space between them up to the edge of the capsules. Each pan has two shoulders, destined to prevent the dilatation caused by heat bringing it into contact with the next higher capsule. The brickwork above the level of the capsules is made of silica bricks; the top cover is made of cast-iron or glass. The acid gases are aspirated by a jet of water, or in other suitable manner, and are condensed or not. The heat of the fire-gases issuing from the apparatus is used for bringing up acid from 50° to 60° B. in a similar apparatus or in lead pans.

One such apparatus is stated by the inventor to produce from 18 to 20 cwt. concentrated O.V. from acid of 60° B. (142° Tw.), with an expenditure of about 13 per cent. of coals of somewhat inferior quality. According to further information received from the inventors, they bring their acid from 53° to 65°·5 B. with 21 per cent. of the same coal; the cost of an apparatus is about £20, all told.

This system is minutely described by Kretzschmar in Chem. Zeit. 1892, p. 418. The gases from a set of four furnaces pass underneath three sets of leads pans, where they concentrate the acid up to 134° to 142° Tw., and heat them to 145° or 149° C. Each furnace produces 25 cwt. of acid of 93 per cent. daily, with an expenditure of 23·5 per cent. of rather low-grade English coal. The breakage of dishes per month was at first 5, out of a total of 64, costing 4*s*. each ; but this was greatly lessened when the cast-iron bed-plates were replaced by fire-clay slabs. The acid vapours from each set of two furnaces pass into a lead condenser, then into a cooling-worm, and eventually into an upright pipe, in which the necessary draught is produced by a jet of compressed air. The Négrier apparatus has the advantage of allowing the use of impure and nitrous acid, but it requires much more space, labour, and coal than platinum stills.

The Négrier apparatus had been erected at the Rhenania works, Stolberg, but was given up as causing too much expense for fuel and breakage of dishes and performing too little work.

F. Benker has erected in France a number of apparatus concentrating sulphuric acid in porcelain capsules, covered with a special protecting cement and heated by several small fires. The whole is enclosed in a chamber built of Volvic lava, and the capsules very rarely break. According to a direct communication from the inventor (1902) he has built many such apparatus with 20 capsules during the last ten years, which have given excellent results. At a Spanish works the consumption of coke has been lowered to 9 parts for 100 acid of 92 or 93 p. c. This acid is much purer than that made in platinum, and perfectly clear. It can be brought up to 97 or 98 p. c., in order to deposit all iron salts; at a French factory such acid (made from Sain-Bel pyrites) is diluted with distilled water and sold for use in storage-batteries. Benker's system is shown in figs. 367 and 368. The capsules are all placed on fire-clay rests and are cemented in these with asbestos and water-glass, so that the fire-gases are altogether separated from the acid fumes. They are cleaned out once every 6 or 8 weeks, and exchanged after 6 or 8 months. By special precautions in manufacturing, they are now made practically unbreakable, but in case of an accident they can be exchanged with a stoppage of only 2 or 3 hours. The acid fumes are condensed in lead-lined boxes filled with bits of stoneware of the size of a pea. The last capsules are not directly heated; this is very important for making 98 p. c. acid, since there is too much dissociation of H_2SO_4


3,50
2,30

if the acid boils too strongly. There is very little distilling acid, and this is only 4° to 8° B. strong, which makes the system very economical. The apparatus consists of two sets of 20 capsules each, and furnishes per day 4½ tons ordinary acid of 66° B. or 3 tons 4 cwt. to 3 tons 8 cwt. of extra concentrated acid (97–98 p. c.); the former with a consumption of 12–15 p. c., the latter with 18–20 p. c. fuel (coke, or a mixture of coke and coal). The cost of the apparatus is about £400, inclusive of the previous concentration to 60° B. in lead pans. The latter are provided with a special fireplace which is used for the start, but is unnecessary afterwards, as the waste heat of the other fires is more than sufficient for heating the lead pans. The bottom capsules rest on fire-clay supports, the top capsules on cast-iron ones. The capsules are covered with a thin layer of fire-proof and acid-proof cement, which can also be used for mending any broken capsules. Such breakages very seldom occur; a new capsule costs about 5*s*. (comp. also Pierron, Monit. Scient. 1900, p. 366).

Similar in principle are *the beaker-apparatus* of Webb, Levinstein, and others. Webb's English patents are Nos. 2343, 17,407, and 18,891, all of 1891. As figs. 369 and 370 (p. 853) show, his apparatus consists of 14 or 16 glass (or porcelain) beakers, A, A, arranged one above the other, about 11 in. wide and 21 in. high, with overflow lips communicating with movable tapering glass pipes placed in a slanting position in the next lower beaker, so that the acid flows from each beaker on to the bottom of the next, and from the last of these through a cooler into the vessels where it is to be stored. According to Webb's patent No. 2343, 1891, a series of glass vessels are placed on slabs, arranged in steps, in a heating-chamber; the vessels are enclosed near their upper edges in iron plates or slabs, corresponding to the bottom. In each of these vessels is placed at an angle a loose tapered glass tube, reaching from the spout of one vessel to the bottom of the next lower vessel, where it is provided on its side with an outlet-slit. The fire-gases pass first into combustion-chambers on one side of the heating-chamber, and from thence into the space left round the glass vessels. The weak liquor is fed into the tube of the uppermost vessel and displaces a certain amount of acid, which will overflow into the tube of the next vessel, &c., thus causing a thorough interchange in the liquor to be evaporated. The concentrated acid is delivered from the last vessel of the series.

Much stress is laid on the fact that the acid always flows on to the bottom of the next lower beaker, where it forces the already concentrated acid upwards and is well mixed with it.

According to the inventor, the cost of an apparatus of 14 glasses, apart from patent royalty, is from £60 to £100. Usually two sets are built together. 14 glasses produce per hour a carboy of acid of spec. grav. 1·838 from acid of 1·74, with consumption of less than ½ cwt. of coke. One man can attend to 4 sets of 14 glasses each, in which case the cost of labour is only 2*d.* per carboy. Each set makes 5 or 6 tons of strong acid per week from acid of 1·60, or 11 to 12 tons from acid of 1·74.

According to actual observation, at first the breakage was very considerable, in fact intolerable, so long as all beakers were made of glass. Very soon the three bottom beakers of each set were replaced by porcelain vessels, by which the breakage was greatly reduced. More recently *all* the beakers have been made of porcelain or of stoneware, and since then the breakage has been very slight. The feed of acid is regulated by means of a thermometer placed in the fourth beaker from the bottom. No lead pans are needed for preliminary concentration. Even the most impure acid, also waste acid from dynamite-works &c., can be worked up. The acid running off in cases of breakage is easily caught and used over again.

A fresh patent of Webb's (E. P. 29,884, 1896) describes a firing arrangement by a gas-producer, where the flame does not act from the higher end down to the lower, but *vice versa.*

The illustrations of Webb's apparatus, published in certain periodicals during 1901, differ from those given here only in two respects: first the fireplace is not below the top beakers, but about midway; second a number of upright pipes take the acid fumes away into a main pipe and lead them into a condenser, where the acid is to be kept back from escaping into the atmosphere.

Webb (E. P. 1515, 1901) also describes an apparatus for retaining the acid fumes, consisting of a wooden box, lined with lead, closed at top, with a funnel-pipe reaching nearly to the bottom for admitting cooling-water, which overflows near the top. The tank contains two metal boxes, connected by a number of pipes, the first of them fitted with several water-tubes. The acid fumes enter at the top of the first box, pass through the connecting-pipes into the second box, and issue from the top of this into a chimney, which produces the necessary suction. On their

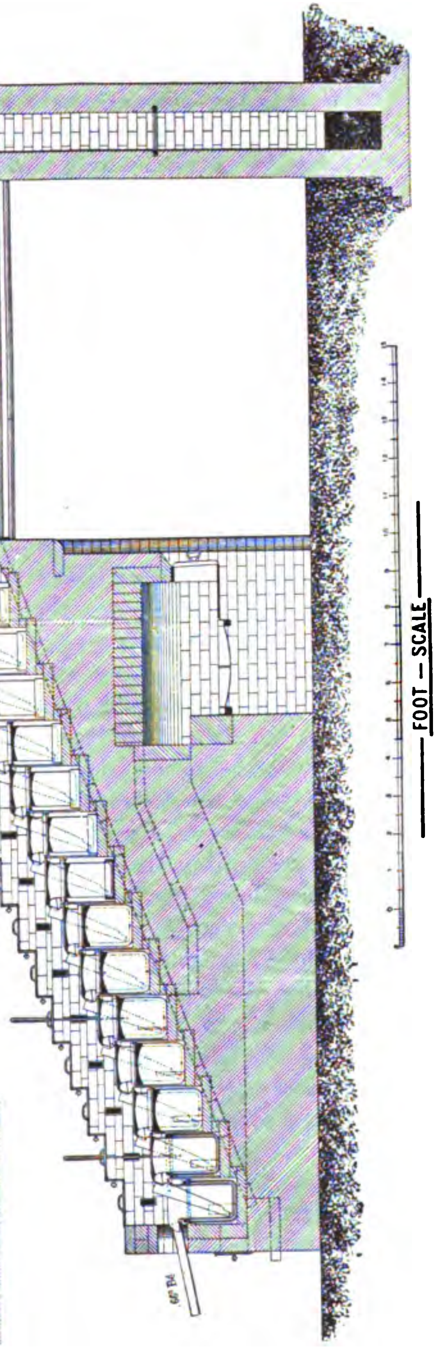


Fig. 369.

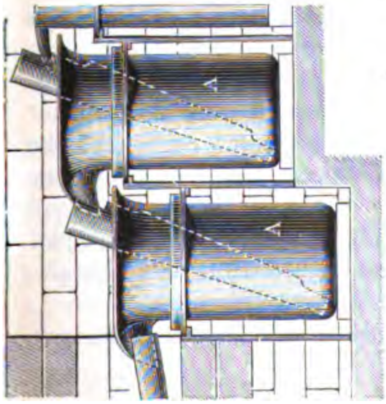


Fig. 870.

way the fumes are cooled by the water surrounding the boxes and flowing through the water-tubes and are thus condensed; the liquid thus formed runs off at the bottom. In order to retain the acid longer in the first box, the pipes connecting it with the second box are furnished with nozzles which throttle the orifice.

A further patent of Webb's (E. P. 1516, 1901) describes beakers consisting of an outer vessel and an inner vertical vessel, the latter having at its lower end lateral openings, and its top reaching above the outlet bib of the outer vessel, for the purpose of dividing the liquid into two columns. There is also a removable spout attached to the top of the beaker.

This modification appears to be that which is mentioned in the 38th Alkali Inspector's Report, and described in the German patent No. 135,886, by F. G. Webb and Webb's Patents Limited. There is a stepped series of beakers, each of them containing an inner cylindrical vessel, not much narrower than the beaker itself, open at the top and communicating by holes at the bottom with the annular space between the two vessels. The acid overflows by a lip from each of the outer beakers into the inner vessel of the next lower beaker, passes through the bottom holes into the annular outer space, and overflows from this into the inner vessel below. The whole may be placed in a hot-air oven. Or else the top edges are formed in such a manner that a still-head may be placed on each beaker, with an arm connected with a slanting draught-pipe [comp. Gridley's apparatus, p. 844], from which the vapours are taken into a tubular water-condenser before passing into the draughting-shaft : in this case the beakers are heated only in their lower part.

Levinstein's patents are: No. 19,213, 1892; Nos. 2476 and 2835, 1893; No. 22,844, 1894; his apparatus is very similar to Webb's, but the beakers have rounded bottoms and are placed in metal dishes, and the overflow-pipes are modified. According to one of his latest patents, the dilute vapours from the upper portion and the strong vapours from the lower portion of the battery are carried away separately, which appears to be a very rational process.

Quite similar to the above is Bradbury's apparatus, Engl. pat. 22,327, 1893; J. W. Scott's, Engl. pat. 14,215, 1894; R. Wilson's, E. P. 14,221, 1895 ; and Schwab's, E. P. 22,512, 1896.

Many of these apparatus, especially on Webb's principle, have been erected in England, but some of them seem to have been discontinued, partly on account of excessive breakage of the glasses (which does not seem to happen so much with porcelain beakers), partly because they consumed too much fuel, and partly because it was found impossible to prevent the escape of dense white fumes from the chimneys (which were themselves sometimes ruined by these fumes and had to be rebuilt). The Alkali Reports of the last years teem with complaints of this sort. The reason seems to be the same as that quoted in the case of the lead pans with surface-evaporation, viz. the formation of an acid mist of tiny, liquid, vesicular drops (p. 812), or else the difficulty of condensing sulphuric anhydride (11th Chapter).

A. Nobel proceeds on the following principle (Germ. patent 10,149, 1880):—Since cast-iron is not acted upon by the *vapour* of sulphuric acid, the concentrating-apparatus is made in the shape of a column consisting of cast-iron pipes, in which porcelain dishes are placed on ledges. Each dish has an opening, through which a glass rod reaches into the next lower dish; this is intended to prevent the acid from splashing about in its downflow from dish to dish. When all the dishes are filled, the column is heated by flues surrounding it on the outside. The acid vapour, as well as the concentrated vitriol, is taken away at the bottom. Even nitrous vitriol is said to be used in such towers.

Another kind of column combined with the system of stepped beakers is the apparatus patented by Guttmann (E.P. 16,220, 1898). He arranges glass or porcelain beakers, with overflows, in a vertical spiral column. They are placed on iron dishes, attached to curved, hinged doors, which together form a vertical heating-column, within which fire-gases surround the concentrating-beakers. Another patent (G. P. 109,247) describes an arrangement for heating up the air required for the combustion by means of the waste heat of the apparatus.

A Guttmann concentrating-tower has been erected in England, but it is fired by coke instead of gaseous fuel, and has been otherwise modified with a view to reduce breakages (Alkali Inspector's Report No. 38, p. 128).

The Adamson Chemical Company (G. P. 104,679) concentrate sulphuric acid in two horizontal stoneware cylinders; a number of vertical stoneware or glass pipes, closed at the bottom, are suspended from these cylinders in a vertical position, reaching downwards into the fireplace and increasing the heating surface. [This is the system of "Field tubes" applied by De Hemptinne in his apparatus described in our first edition, Vol. I. p. 507 *et seq.*, which has never been carried out in practice.]

Concentration in Platinum Stills.

The arrangement of platinum stills formerly employed is very fully described and illustrated in the first edition of this work, pp. 526 to 530, and in our second edition p. 695 *et seq.* A number of data referring to the sizes, cost, and producing-power of those older stills is also there given; but all this must be considered antiquated, and we shall here describe only the modern shapes of platinum stills.

In consequence of competition with the platinum stills, first by the improved glass retorts, and afterwards by the combined platinum-lead apparatus of Faure and Kessler, the two manufacturers of large platinum apparatus (Desmoutis, Lebrun, & Co., of Paris, and Johnson, Matthey, & Co., of London) both greatly improved the construction of platinum stills. In the first place they made them lighter, by leaving the greatest strength entirely in the bottom, directly exposed to the fire. Already in 1867, Johnson, Matthey, & Co. had exhibited at Paris an apparatus for 5 tons per diem, costing only £1640, and another for 8 tons per diem at £2500.

Later on they recommended a lighter shape of still, intended for continuous work. A double still of that kind, for producing 4½ or 5 tons concentrated acid per day, cost £1200, a triple still, for 7½ or 8 tons acid, £1750. Then stills with their special cooling-apparatus found much favour, but they are equally out of date now.

The modern platinum stills are mostly on the system of Prentice or of Delplace, as shown here.

Prentice's system (figs. 371 to 373) contains, in lieu of the former circular stills, a still of elongated square shape, say 3 ft. × 1 ft. 6 in. for 4 or 5 tons O.V. per day. The acid enters at the back end and runs out in front by an overflow. A still of this kind weighs about ½ cwt., and cost (formerly) about £1000, inclusive of overflow, cooler, metal ring, &c. The firm also supply platinum pans with corrugated bottoms, as shown in fig. 371; but ordinary lead pans may be used instead.

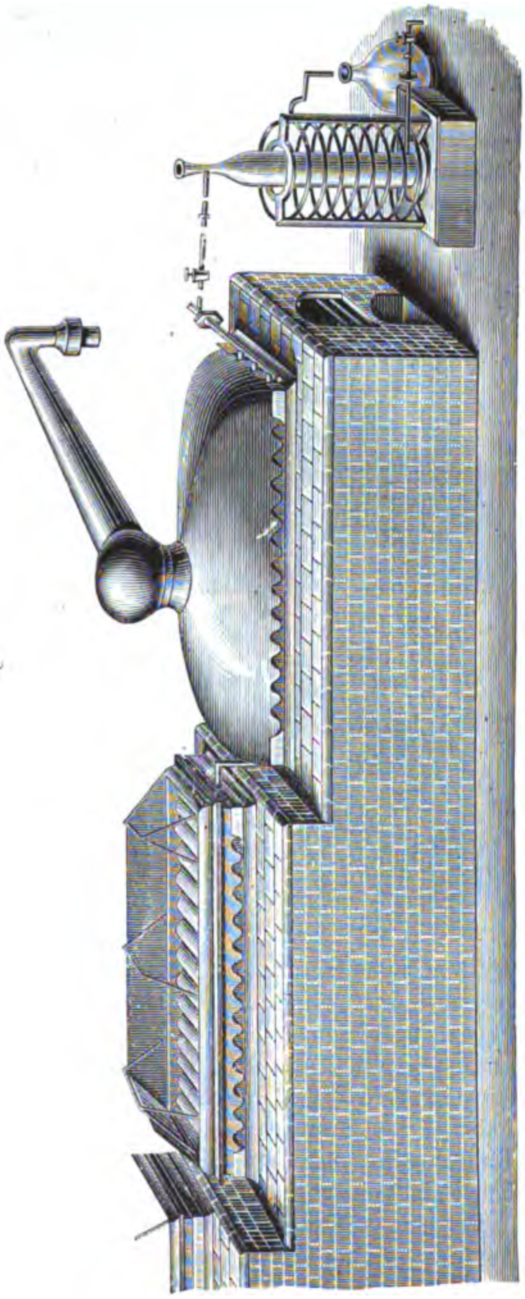


Fig. 371.

Special statements concerning these stills, as introduced at the Griesheim works, will be found in 'Chem. Ind.' 1878, p. 194, and 1879, p. 109.

The favourable effect produced by Prentice's plan is principally owing to the corrugated bottom of the pans, which increases the heating-surface in the proportion of 1·57 to 1. The thin stratum of acid is a feature common to all more recent plans.

Fig. 372.

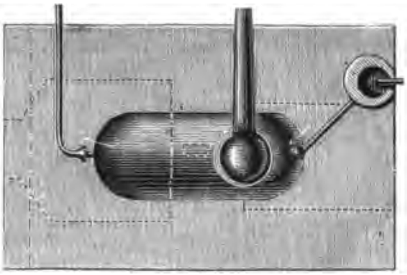
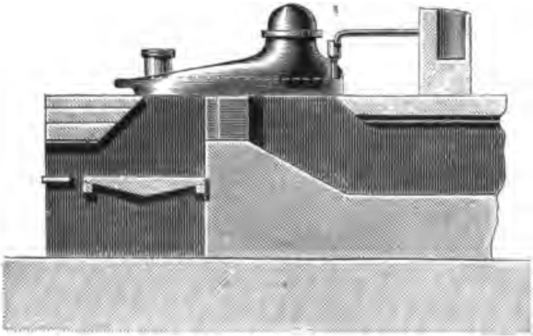


Fig. 373.



Another system, manufactured by Messrs. Johnson, Matthey, & Co., and introduced at some of the largest works, is that of Gustave Delplace, of Namur, which is shown in figs. 374 to 376. In this apparatus two stills, A and B, are combined. The top still A is fed with acid of 144° Tw. and the distillate from the still B. The latter, also of platinum, carries on the concentration to the highest attainable point, even up to 98 per cent. H_2SO_4, if needed.

C C are heads and arms with outlet at E for the strong distillate; the weaker not condensed vapour goes away at E. F is a bottle-shaped cooler for receiving the concentrated acid from the stills.

G is a lip attached to the first still for receiving the acid from the lead pans and the distillate from B B. H is a tube for receiving the condensed distillate and carrying it back to A A. In this apparatus the acid may be brought to 79 or 80 per cent. SO_3, or 97 to 98 H_2SO_4. If this stronger acid, indispensable in the manufacture of dynamite &c., is made, the distillate must be allowed to get up to 150° or 155° Tw., and is always conveyed back to the first still. For making the ordinary O.V., testing 168° Tw., which really contains only 73 to 76 per cent. SO_3, the distillate should show only 7° to 23° Tw., according to the speed of work, the feed-acid being 144° Tw. strong. The following advantage is claimed for the rectangular shape of still—that, in working for the most highly concentrated acid, the ferric sulphate cannot collect in the opening of the discharging-pipe, which generally happens with the ordinary apparatus; the distillate is also said to be weaker, the output larger, in proportion to the evaporating surface, and the consumption of coal smaller than with the round shape. Instead of lead coolers, the distillate is condensed by a platinum tube 2¼ inches wide, which is cooled by water for a length of 5 feet; together with the head it weighs no

Fig. 374.

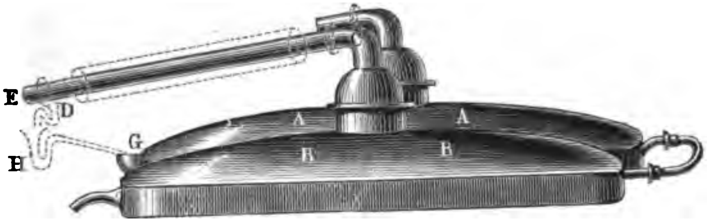
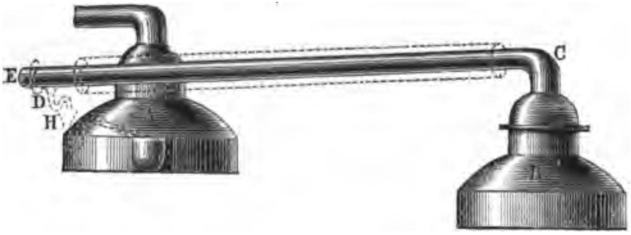
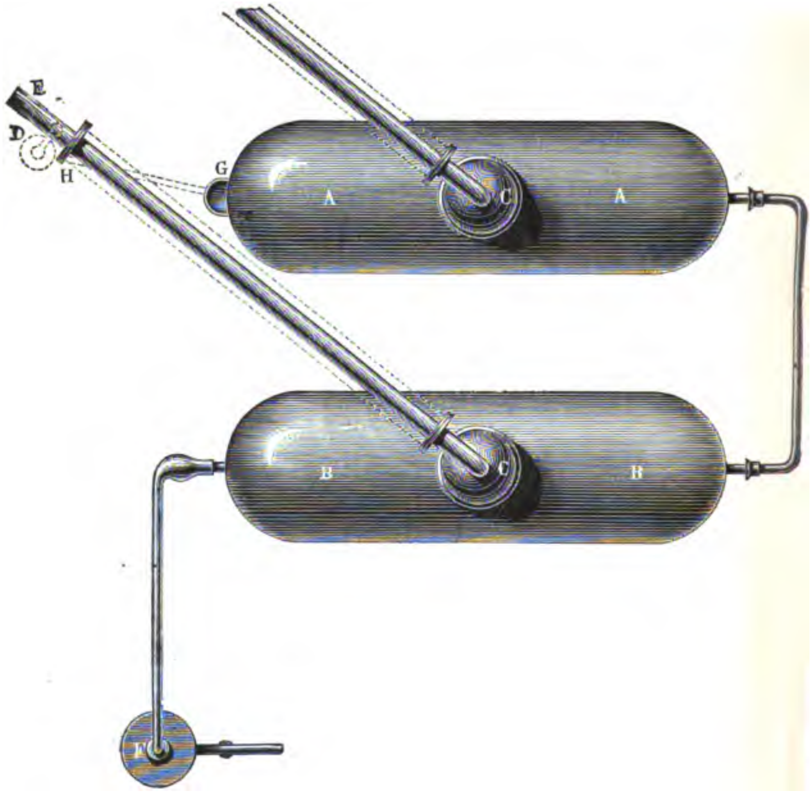


Fig. 375.



more than the former large head and arm for connection with a lead cooler, without being liable to the frequent need of repairs of the latter; it also permits condensing acid of any strength, free from lead. Consequently the concentration may be carried to any required extent, whilst with lead condensers, and still more with Faure and Kessler's system, the great wear and tear of the lead do not permit this.

Fig. 376.



For making the very strongest acid by a continuous process (which previously was quite impossible), two long stills are preferable to one, the distillate from the second still running back into the first quite hot, without contact with lead; only the first weak distillate escapes.

The cooling of the concentrated acid is done by an upright platinum cylinder standing in water. The acid enters at the top and leaves it at the bottom; the water enters the outer vessel at the bottom and leaves it near the top.

Fig. 377.

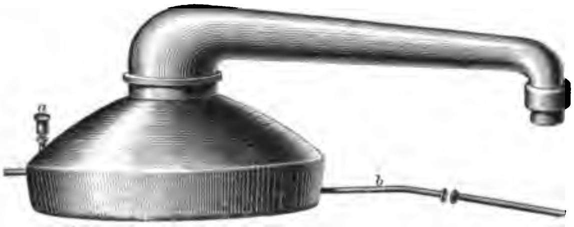


Fig. 378.

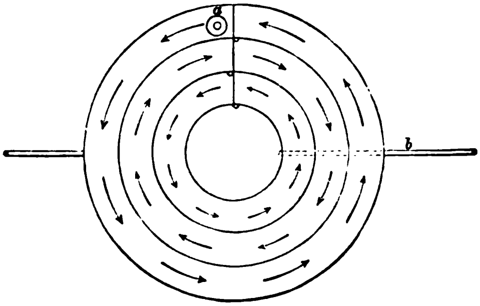
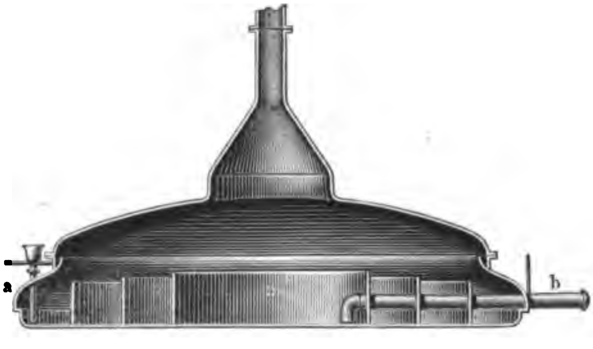


Fig. 379.



The apparatus is supplied by Messrs. Johnson, Matthey, and Co. by weight, at market prices for platinum. The weight of one boiler is about 50 lb.; head, condenser, and acid-cooler together 17½ lb. With this 5 tons of acid of 93 to 94 per cent. monohydrate, or

6 tons of 92 per cent. monohydrate (the common "168° Tw."), are made. A two-boiler apparatus, weighing about 110 lb. with all appurtenances, furnishes 10 tons of O.V. at 93 to 94 per cent. or 12 tons at 92 per cent. in 24 hours. M. Delplace (Ste. Croix 7, Namur) undertakes the erection and starting of the apparatus.

Some improvements have been made in his apparatus by Delplace's patent of 1882 (G. P. 23,159). He provides a long, flat platinum still with an undulated cover, bearing on the top of the four undulations as many still-heads. From that which is nearest to the acid feed, only water distils off; the others yield water with more and more acid, the fourth rather strong acid. Thus with one pan acid of 98 per cent. H_2SO_4 can be obtained. The bottom is best made in a corrugated shape (as on p. 857). I am not aware whether this kind of still has been carried out in practice.

Fig. 380.

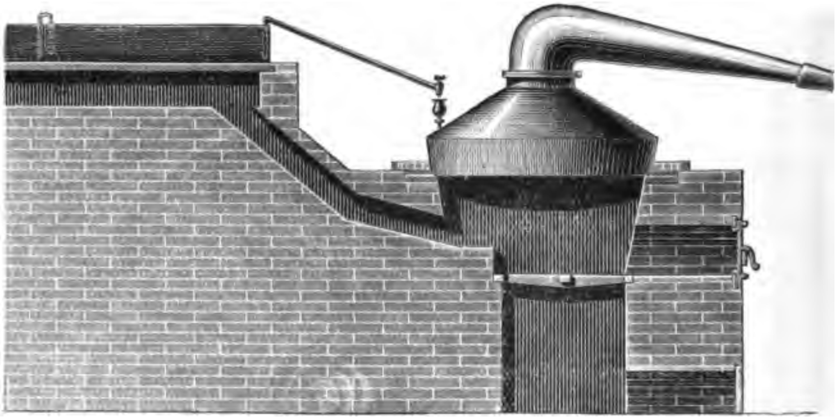
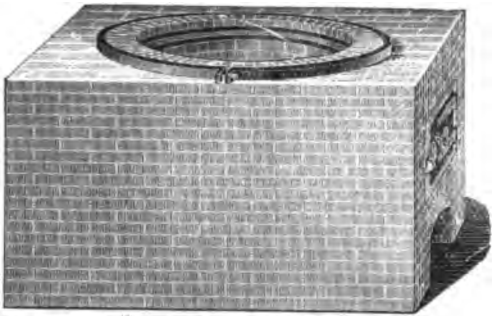


Fig. 381.



The platinum stills built by the Paris firm F. Desmoutis, Lemaire et Cie., as formerly used, before the shallow form had been introduced, are shown in the first edition of this work, Vol. I. pp. 526 and 536. Since 1876 this form has been replaced by a shallow still, as shown in fig. 377; and this is frequently made with a bottom fitted with concentric partitions, which force the acid to travel through the still in a circuitous way, as indicated by the arrows, and ultimately to flow out through pipe *b*. This is shown in figs. 378 and 379 (p. 861).

Fig. 382.

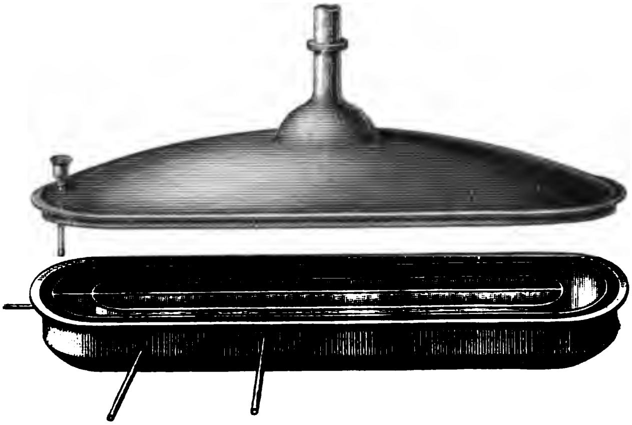
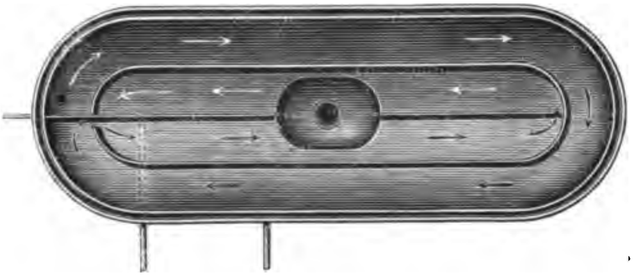


Fig. 383.



(It must not be overlooked that these partitions are sometimes found to leak, which has caused some manufacturers to abandon this otherwise very rational plan and to return to plain-bottomed stills.)

The latter figure shows a special modification, provided with a removable cover, hydraulically sealed. Figs. 380 and 381 show the setting of these stills, which is extremely simple, the still-bottom resting on a plain cast-iron ring.

Figs. 382 and 383 show a longitudinal still, recently preferred by some French manufacturers, equally provided with partitions. Formerly most buyers preferred the circular shape; now some of them prefer the oblong shape as better utilizing the fuel. But common to all are the partitions which cause the acid to flow through the still in a prolonged stream, without any mixture of the concentrated with the dilute acid. This system has now been applied for 15 years with great success. Where two stills are to be worked in combination a difference must be made between the case where acid of 65½° B. and that where acid of 97–98 per cent. is required. In the former case it is best to place both stills on the same fire. They thus produce slightly less than if fired separately; but this is outweighed by the saving in fuel, labour, and repairs (about 20 per cent. on the fuel and 25 per cent. on labour and repairs). The waste fire-gases cannot concentrate the feeding-acid in the lead pans, which these receive from the chambers, above 59°·5 B. (=140° Tw.); but this is an advantage, as the acid gets less charged with lead, and its strength is absolutely regular. The quantity of distilling acid is lessened; the finishing still furnishes a distillate of from 20° to 25° B. (=32° to 42° Tw.), whilst the distillate from the first still is almost pure water and is thrown away. This combination is shown in figs. 309 and 310 (p. 709) of our second edition; the two stills, all complete with a Liebig's cooler, weigh 50 or 51 kilog. for a production of 10 tons in 24 hours.

For concentrating acid up to 97 or 98 per cent. H_2SO_4 two stills must be combined, each of them heated by a separate fire.

(This system, as well as other shapes of these French stills, is illustrated in our second edition.)

Scheurer-Kestner (Bull. Soc. Ind. Mulhouse, 1892, p. 321) gives data concerning the difference produced by working with a Desmoutis still, first without and then with concentric partitions, the acid being forced by the latter to remain longer in the stills in the proportion of 48 : 62. The data refer to both styles of work :—

	Without partitions.	With partitions.
Make in 24 hours	5136	6632 kil.
Concentration of acid	92·5	92·5 per cent.
Average strength of distillate ...	36°	11° Baumé.
Weight of ditto	2160	2160 kil.
Weight of the corresp. H_2SO_4...	816	216 ,,
Percentage of acid distilled......	15·8	3·2
Weight of coal used	1100	1100 kil.
Ditto per cent. conc. acid	21·4	16·5
Water evaporated..................	1344	1944 kil.

These undoubted advantages of the concentric partitions are, however, counterbalanced by a greater loss of platinum and more frequent repairs, so that many manufacturers have abandoned this system after having tried it.

The way of firing platinum stills is of the greatest importance, not merely so far as economy of fuel is concerned, but even to a greater extent where it is necessary to manufacture acid of a regular and high degree of concentration. Ordinary hand-fired grates will do quite well where the acid need not exceed 95 per cent. H_2SO_4 ; and the waste heat of the flame may be utilized for bringing up the chamber-acid in lead pans to the strength required for feeding the still, say 140° Tw., although in most cases this can be equally effected without any cost by the waste heat of the pyrites-burners. But where acid of 96 per cent. is regularly required, it is much better to adopt a plan ensuring perfect regularity of heat; and this becomes indispensable when acid of 97 or 98 per cent. is to be regularly run in a continuous process. This is very easy to understand, for with the very shallow depth of acid now universally employed a slackening of the fire will instantly tell upon the concentration. Supposing the feeding-acid to be of uniform strength (a necessary condition for continuous work), it stands to reason that the strength of the acid run out in a continuous process must vary with the heat employed, and that consequently that heat should also be as uniform as possible. No ordinary fire-grate will fulfil this condition; this may be done by really efficient mechanical stokers; but I am not aware of any case where such have been tried for platinum stills. Another means for attaining the same end is the employment of good gas-producers, and of these the most efficient for the present case seems to be that of G. Liegel, of Stralsund (Prussia). A large number of Liegel producers have been already fitted to platinum stills and have been working for many years past; and I am assured, on most reliable authority, that there is nothing equal to them for obtaining the most highly concentrated acid in a regular way. Figs. 384–389 show the Liegel producer as applied to sulphuric-acid stills; but, of course, special modifications must be made in particular cases, as stated by the inventor of the system.

In Knocke's description of the Oker works (Dingl. Journ. cliv. p. 181) it is mentioned that formerly the platinum stills used to be fired with coals, but that wood had been introduced instead, because the still was found damaged in consequence of the sulphur contained in the coals. Even by the formation of carbon-platinum the platinum may become brittle; the fuel, therefore, ought never to come into immediate contact with it.

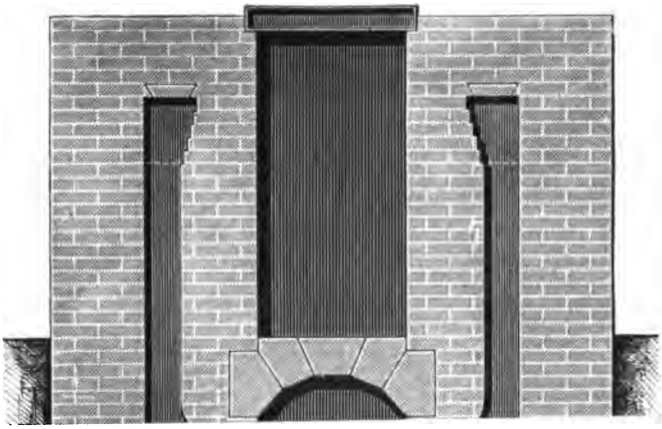
Fig. 390 gives an idea of the way in which platinum stills can be set so as to avoid all risk of damage by silicates from the coal-ashes being projected against the pan-bottom, or other damage by the fire (received from Mr. W. C. Heraeus, Hanau).

Concentration in Platinum Dishes with Lead Hoods (Faure and Kessler's system).

The first stills constructed on the principle of combining a platinum bottom-dish, as the only part of the still coming in contact with the hot concentrated acid, with lead covers cooled by water were used by Messrs. Harrison, Blair, and Co., of Bolton, and Mr. A. Smith, of Dublin, some time before 1860, but were given up again. In 1863 L. Kessler proposed his first still, which was erected at Griesheim (Dingl. Journ. vol. clxxvi. pp. 34 & 164, ccxxi. p. 85). This apparatus was not a success, and was replaced 10 years later by the firm of Faure and Kessler, at Clermont-Ferrand, by a new construction which itself has been gradually changed as more experience was gained. The older forms of the apparatus, which are not used now, are fully described in our first edition pp. 542–551, with many illustrations. We shall here only describe the present form of the apparatus, with the aid of detailed drawings to scale, kindly furnished by the proprietors

[*To face* p. 866.

Fig. 386.



ated and described in detail further on. The dilute acid con-

of the patents, Messieurs F. Desmoutis, Lemaire et Cie., of Paris, platinum works.

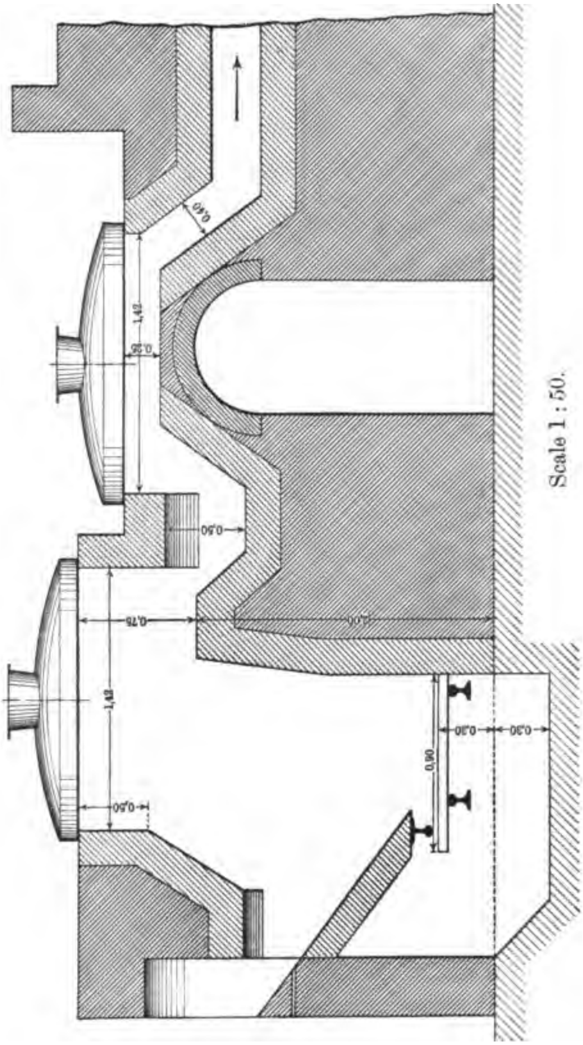


Fig. 390.

Fig. 391 gives a general sketch of the apparatus on a scale of $\frac{1}{25}$. *a* is the platinum basin, with the lead bell *b*, which will be illustrated and described in detail further on. The dilute acid con-

Fig. 392.

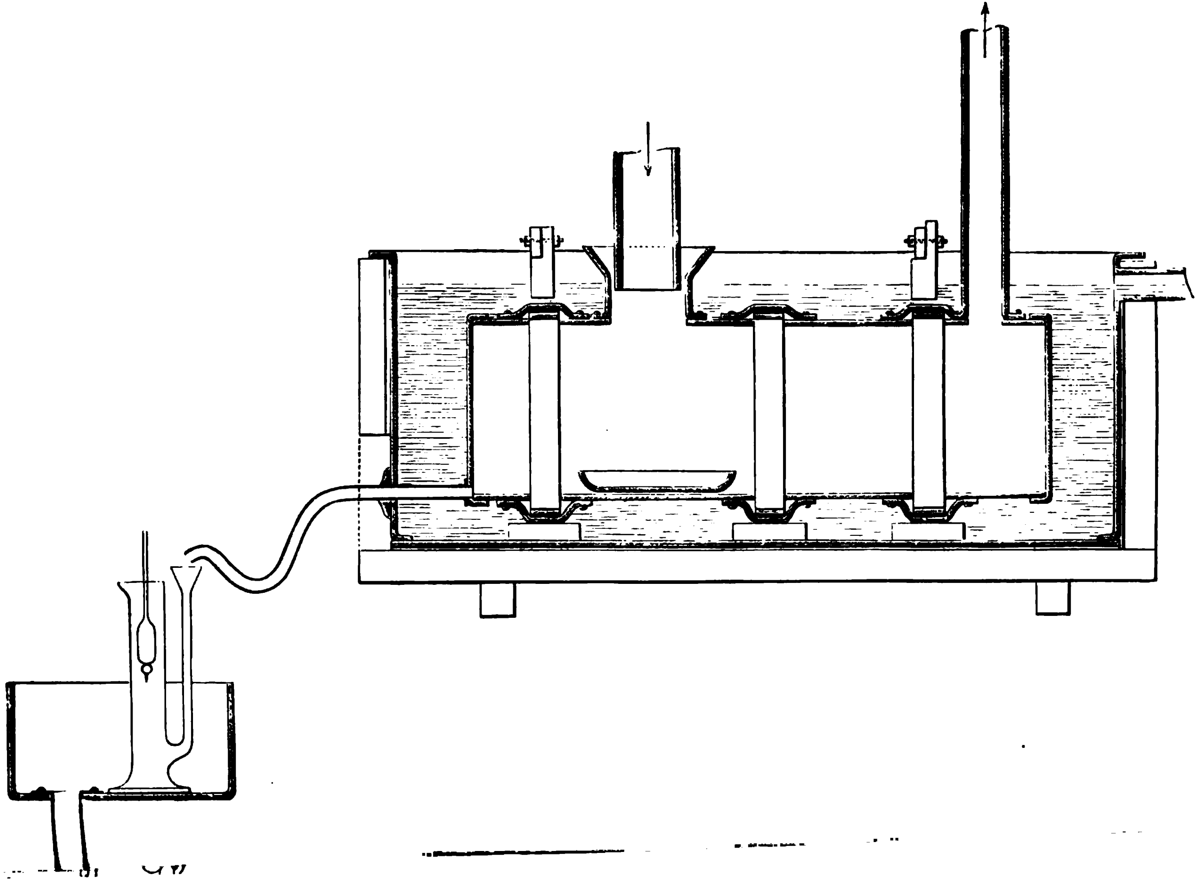


Fig. 392.

densing on the sides and top of the bell runs away through pipe *c*. The uncondensed vapours pass away through pipe *d*, which bends downwards and dips into the condenser *e*. The acid formed here, after passing through the hydrometer cylinder *f*, runs away through *g*, together with that from *c*. The cooling-water for the bell enters at *h*, that for the top cover at *i*. The concentrated acid runs away at *k* into the cooler *l*, to be described below, and from this through *m* into carboys, &c.

The fire of the fireplace *n* passes either underneath another or even a third platinum basin, each of them placed so much higher than the preceding that the acid can run from one to another, or else directly under a set of lead evaporating-pans, in which chamber-acid of 106° Tw. is brought up to 142°, the proper strength for feeding the platinum basins.

Fig. 392 gives details of the condensing-apparatus for the weak acid, which can be understood without further explanation.

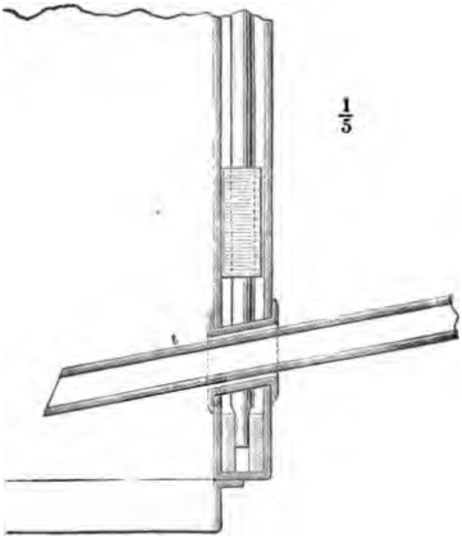
Fig. 393 gives a detailed drawing of the dish and bell, on a scale of $\frac{1}{10}$. *a* is the platinum basin, the size of which must be proportionate to the production intended. In order to stand the work for a considerable time, it should not be too thin; it is necessary to calculate from 2·9 to 3 kilog. of platinum to each ton of 94 per cent. acid made in 24 hours. For instance, a basin capable of turning out 5 tons of strong acid per 24 hours weighs from 14·5 to 15 kilog., and has a diameter of 0·88 metre (= 2 ft. 10⅝ in.) ; for 7 tons of acid it would weigh 20 or 20·5 kilog., with a diameter of 1·06 metre (=3 ft. 5¾ in.) ; for 1½ tons of acid 6·5 kilog., with a diameter of 0·60 metre (=1 ft. 11⅝ in.).

The rim of the basin is shaped like a hydraulic lute, *b b*, with the outlet-tube *c* for the dilute acid condensing on the sides of the leaden bell, *g g*; this rim is supported by a cast-iron ring, *f*. Further there is an outlet-tube, *d*, for the strong acid, and a supporting ring *e* (of cast-iron) for the lower part of the basin.

The basin is surmounted by a leaden bell, formed of a double-walled cylinder, *g g*, and a double-walled conical hood, *h h*. The cylindrical part is supported on the outside by three iron stanchions, *i i* (comp. also figs. 394 and 395), and an iron hoop, *k k* (40 × 5 millim.). The pieces *i i* end at the top in hooks, which serve for suspending the bell, *g g*, by means of chains.

The diameter of the cylindrical part is 0·870 metre (= 2 ft. 10¼ in.) inside and 0·940 (=3 ft. 1 in.) outside. The inner shell has a thickness of 5 millim. (say 11 lb. per superficial foot), the outer 3 millim. (say 7 lb.). Iron rods, *l l*, ½ an inch thick, held by means of straps, *m m*, form a skeleton frame for stiffening the inner cylinders; they are from 3 to 4 inches apart. The pipe *n* serves for introducing cold water in the bottom of the annular space between the two leaden cylinders; pipe *o* conveys the partially-heated water into the annular space of the conical hood, *q q*, and pipe *p* is the outlet for the hot water from the latter. Pipe *r* lets off the air escaping from the cooling-water during its passage through *g g*, and pipe *s* serves for the same purpose in the hood *q q*. The arrow *t* shows where the feeding-acid runs in; fig. 394 gives the detail of this.

Fig. 394.

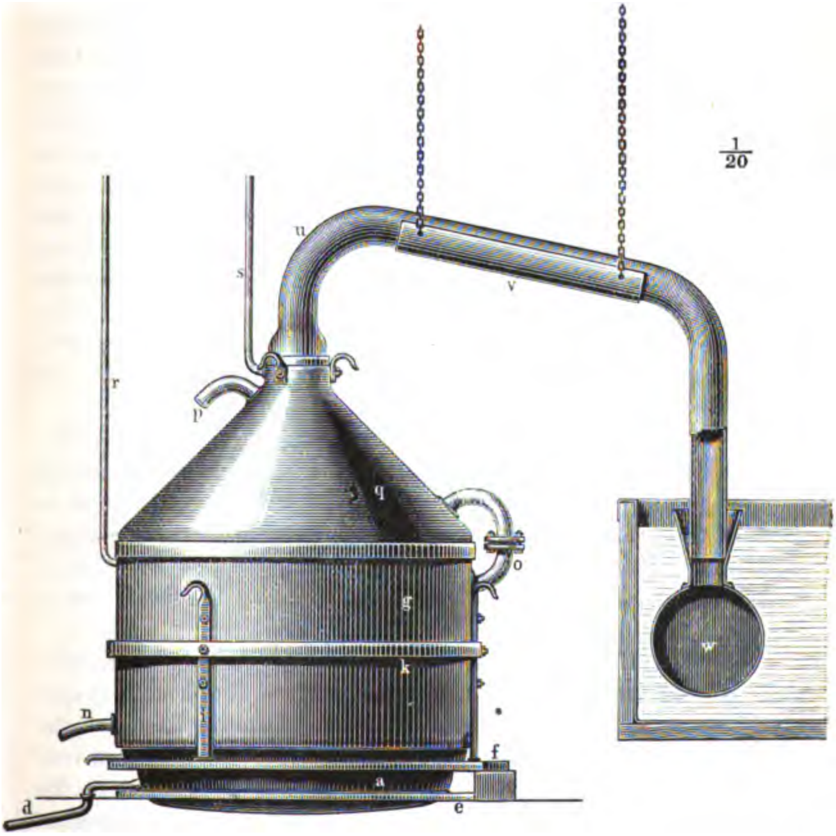


The uncondensed vapours are taken away by pipe *u* suspended from the roof by means of the spout *v* (fig. 395); it dips into the cooler *w*, where the weakest acid is condensed.

Fig. 395 gives a front elevation. The letters all have the same signification as in fig. 391. (Some other illustrations of this system are given in our second edition.)

The *cooler* employed by Faure and Kessler for the strong acid is made of lead, avoiding the use of platinum, and is shown in fig. 396 (p. 873). A lead vessel, A, stands on an annular lead cylinder, B, whose base *b* is a little widened out for greater stability. In the middle of the height the partition *c* cuts off the top from the bottom cylinder, the hollow space of A still remaining in commu-

Fig. 395.

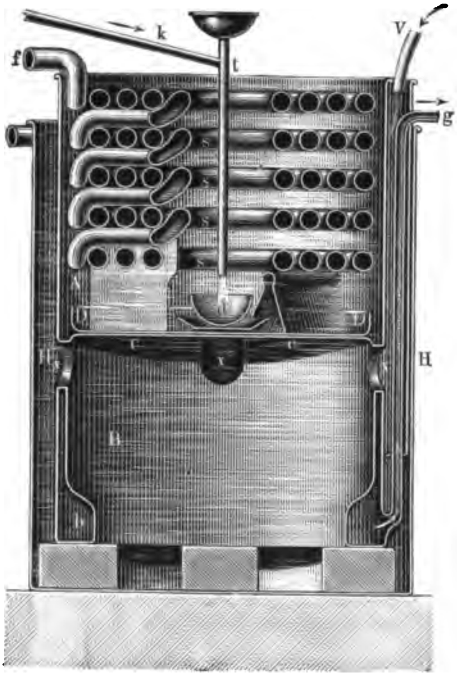


nication with the annular space of B. All the hollow spaces are filled with acid. On the bottom *c* the shallow lead dish D is placed; and in its centre the porcelain dish *d* receives the almost boiling acid from the platinum tube *k*, so that the hot acid mixes with cooled acid without injuring the lead at the point of contact. In A there are five worms, *s s*, connected with each other and constantly fed with cold water, which runs off heated at *f*. The whole cooler stands in a cylindrical vessel H, also constantly supplied with cold water through V ; the latter, therefore, always fills the inner space *b* of the annular vessel B, circulating through the openings *x x*. Since the acid entering through the tube *t* is much hotter than that into which it flows, it rises to the top, comes into contact with the worms *s s*, and is partly cooled ; it then flows downwards along the sides, and passes into the annular space *b*, where it only forms a thin layer and is further cooled. At last it rises up in the pipe *g*, and from this runs into the carboys. As the diameter of the vessel is about 3 feet 3 inches, the stream of acid moves very slowly in it, and there is time for cooling. A cooler of the above diameter and equal height suffices for 100 carboys of acid per diem. This apparatus is very ingeniously constructed, but rather complicated. It requires an excellent plumber and incessant cooling with cold water; otherwise it would be very soon destroyed.

A weak part of the apparatus consists of the lead hoods.—The Chemische Fabrik Rhenania (Germ. pat. 64, 572) makes these hoods of a long coil of lead tubing, burning the walls together so as to form a tight bell, within the walls of which the cooling-water circulates. This system answers very well, and has been introduced at a number of factories. It is probably the best now in existence for this special purpose.

The principal feature of the work with the Faure and Kessler stills is this—that the acid, coming hot from the leaden evaporating-pans, is continuously run into the platinum basin, or the first of a set of two or three such basins, where it stands in a very shallow layer (two or three inches deep), and is exposed to the direct action of the fire playing upon the whole of the bottom of the dish. This causes such rapid evaporation that the acid, issuing at the side opposite to that from which it had entered, and from the bottom of the still, flows out in a sufficiently concentrated state. The amount of work done is proportionate to the size and number of the platinum basins. The mixed vapour of acid and water formed in the basins, as it rises up, strikes against the water-cooled sides and top of the leaden hood, and is there condensed to diluted acid, running down the sides and forming a hydraulic lute between them and the platinum dish; an overflow (at *c*) carries it outside, and prevents it from getting back into the platinum basin. The water-cooling at the same time prevents the leaden hood from damage by the joint action of heat and acid vapours.

Fig. 396.



The cost of fuel is not perceptibly different with Faure and Kessler stills from that of ordinary platinum stills; and the large quantity of water required for cooling-purposes in the former system is an item of cost to be put against the saving which attends the cost of plant. It was urged by the inventors as a great advantage of their plan that the loss of platinum was much less than with stills made entirely of platinum; but this is very doubtful, as the wear and tear of the platinum occur almost entirely in the places which are in contact with the fire-gases, and which are equally large in both systems; and any slight loss of platinum in the other parts of ordinary platinum stills will cost hardly less than the repairs of the very complicated leaden hood and connections of the Faure and Kessler system. According to information from Messrs. Desmoutis, Lemaire et Cie., the bell and hood last about two years, and must then be replaced.

I have also obtained the following data from the same firm. The plumbing work for a F. & K. apparatus turning out five tons of acid of 168° Tw. per diem amounts to about 1200 francs, viz.:

For the bell itself	450 francs.
For the acid-cooler	350 „
For the vapour-condenser ...	250 „
For sundries	150 „
	1200 „

or about 1 franc per kilog. of the lead employed.

The consumption of cooling-water averages 3 tons per hour, or 75 tons per day.

The consumption of fuel is from 18 to 20 per cent. of the acid manufactured.

The great saving in prime cost caused a rapid spreading of the Faure and Kessler system, especially in Germany, Austria, and America, much less in France and England. But since the ordinary platinum stills (owing, no doubt, to the stimulus given to the makers by the new system) were considerably improved, and were constructed of much lighter weight and cost for the same output than formerly, and since the drawbacks of constant repairs, of the great amount of water required, and the frequently minor strength of the acid produced in the Faure and Kessler stills became more perceptible, the latter system has again receded into the background, although, of course, the apparatus once erected are still kept at work. There are probably few new stills constructed according to this system, and several manufacturers who had put up this apparatus have replaced it with ordinary stills *. The enormously increased price of platinum might give a new impetus to the Faure and Kessler system, if L. Kessler's own new hot-air apparatus did

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* This is confirmed by information received from platinum-smelters in 1902.

not seriously compete with his former invention (comp. later on). It must not be overlooked that the strength really attained by it rarely exceeds 93 per cent. H_2SO_4, or at the very most 96 per cent.; with higher strengths the lead hood is acted upon to a perceptible extent.

Other forms of Platinum Stills.

We here briefly quote a number of patent constructions none of which have found any, or only very little, application beyond the places where they originated.

A still constructed by F. W. Kalbfleisch is figured and described in our 2nd edition pp. 722 to 724. It was patented in Germany in 1877 (No. 1005) and improved as described in the U.S. patent No. 267,221 (J. Soc. Chem. Ind. 1883, p. 42). Other American stills are those of M. Willett (E. P. 9362, 1884); C. Bartsch (E. P. 6127, 1885); Herreshoff, H. Nichols and G. Nichols (E. P. 1998, 1887). We mention also H. Glover's platinum dish, placed within the gases of a brimstone-burner as shown p. 281.

Siebert (Engl. pat. 9514, 1893) built platinum retorts with stepped bottoms, on which the acid runs down in cascades. [The rate of concentration and the consumption of coal are very favourable in this apparatus; but it has been abandoned, as the bottom could not be prevented from running dry, and thus the wear and tear became too great.]

Hannetelle (Engl. pat. 22,704, 1891) describes four cylinders mounted stepwise, inclined alternately to opposite sides, the acid running downwards through all of them. The "Chapuis still" is constructed on the same principle.

Lasne uses a flat, oblong still, 6 ft. 6 in. long, in which the acid runs from one end to the other in a layer of about 2 inches.

Howard (E. P. 1762, 1897) describes an automatic apparatus for regulating the strength of the acid flowing out of the platinum stills.

England (E. P. 22,715, 1895) employs the heat of the outflowing acid usefully, by cooling it with the fresh acid to be concentrated.

Loss of Platinum in the Concentration of Sulphuric Acid.

This is a very important matter, on which the first accurate observations were made by Scheurer-Kestner in 1862 and continued for many years. Detailed statements regarding this subject are given in our second edition, pp. 725 to 727. Here we give only a brief abstract.

In the presence of small quantities of nitrogen acids, the loss is from 2 to 3 grams platinum per ton acid of 93 to 94 p. c. H_2SO_4, in the absence of these (removed by ammonium sulphate) only a little over or under 1 gram. "Extra-concentrated acid" (97–98 p. c. H_2SO_4) entails a loss of 6 to 8 grams platinum per ton. The head, siphon, &c. also suffer a loss of weight.

Hasenclever gives the loss of platinum when using acid free from nitrogen compounds, =0·25–0·97 gram per ton of acid. At Uetikon a Faure and Kessler apparatus lost 0·75 gram per ton of ordinary acid; when making the strongest acid the loss amounted to 10 grams per ton of acid.

Davis (Journ. Soc. Chem. Ind. 1894, p. 210) states that the loss of platinum sometimes diminishes to 0·34 gram per ton. Formerly it was less than it is now [?]. When making 97 per cent. acid the loss occasionally rises to 20 grams platinum per ton (*vide infrà*).

The following information was obtained in 1902. A collection of statements emanating from a number of firms, made by W. C. Heraeus, shows the loss of platinum per ton of strong acid manufactured as follows:—

(1) Concentration to 92 per cent. H_2SO_4, from 0·18 to 0·78 gram.

(2) Concentration to 93–96 per cent. H_2SO_4, from 0·30 to 1·3 gram.

(3) Concentration to 97–98 per cent., 1·9 to 3·0 grams.

Undoubtedly the durability of platinum stills is greatly influenced by the way they are set and worked. If the stills are placed too near the fire-grate, or if the flame is sooty, compounds of platinum with carbon, silicon, and hydrogen are formed, which make it crystalline and brittle and impart a rough surface to it. In this respect gaseous fuel is superior to every other kind of firing (comp. p. 865; also Knocke's statements, p. 866).

Mercury is sometimes contained in blende &c., and gets into sulphuric acid (p. 781). If it reaches the platinum stills it may do great harm, as it may there be reduced to the metallic state.

Prices of platinum stills.—Hasenclever (Chem. Ind. 1892, p. 30) gives the following table of prices (in marks) of platinum stills per kilogram (the mark = nearly 1*s*.):—

Year.	Marks.	Year.	Marks.	Year.	Marks.
1869	600	1877	798	1885	1040
1870	600	1878	825	1886	1040
1871	600	1879	900	1887	1040
1872	600	1880	880	1888	1080
1873	837	1881	880	1889	1107
1874	837	1882	890	1890	1970
1875	800	1883	947	1891	1650
1876	800	1884	1013	1892	1250

I can continue this list, from statements made to me by W. C. Heraeus, of Hanau. The prices of platinum (to which about 50 marks per kilogram must be added for workmanship in the case of platinum stills) have been:—

Year.	Marks.	Year.	Marks.
1893	1300	1899	2200
1894	1300	1900	2450
1895	1500	1901	2600
1896	1600	1902 (March)	2650
1897	1650	1902 (Dec.)	2600
1898	1800		

Gold-lined Platinum Stills.

W. C. Heraeus, of Hanau, found that *gold* resists boiling sulphuric acid much better than platinum. He quotes the following figures, putting the loss of weight of chemically pure platinum = 100:—

Technically "pure" platinum	90
Alloy of 90 platinum + 10 iridium	58
Pure gold	13

Which means that pure gold suffers only one-seventh as much as technically pure platinum. At the same time, when 1 kilog. of platinum (worth, say, £90) is dissolved, only 144 grams of gold (worth £20) would be lost.

Since pure gold is, of course, too dear for manufacturing stills, Heraeus at his works prepares platinum coated with a firmly adhering layer of gold in the following manner (invented by his chemist, Dr. Kuech):—An ingot of platinum is brought to a white heat exceeding the melting-point of gold, then a quantity of melted pure gold corresponding to the desired thickness of the coat is poured over it, and the double ingot thus formed is rolled into a sheet. Such sheets are made of the following thicknesses:—

0·4	millim.	platinum	0·05	millim.	gold.
0·4	„	„	0·1	„	„
0·3	„	„	0·2	„	„

Both under the hammer and in the fire these double sheets behave exactly like one metal; they are easily soldered with sheet platinum by means of gold, the operation being conducted in such a manner that the layer of gold is melted only at the soldering joint. It is not possible to substitute a cheaper metal for platinum (as, for instance, proposed by Neuerburg, G. P. 58,511), as in this case the slightest injury to the layer of gold would make the apparatus entirely useless, repairs being out of the question. These gold-plated platinum bottoms are especially useful in the manufacture of the strongest (97 to 98 per cent.) oil of vitriol, in which the platinum is energetically acted upon.

According to statements collected by Mr. Heraeus from various firms the loss of weight in his platinum-gold stills per ton of strong acid made (comp. similar statements concerning ordinary platinum stills, p. 876) has been: (*a*) in the manufacture of 92 per cent. acid, from 0·011 to 0·072 gram; (*b*) in the manufacture of acid of 93 to 96 per cent., from 0·03 to 0·138 gram; (*c*) in the manufacture of acid of 96 to 97 per cent., from 0·17 to 0·205 gram; (*d*) in the manufacture of acid of 97 to 98 per cent., from 0·048 to 0·26 gram.

Since 1891, when these apparatus were first brought out (Germ. pat. 63,591), up to the beginning of 1902, 73 platinum-gold stills have been sold to 16 works in Germany, 18 to 7 works in Austria, 21 to 8 works in America, 7 in Russia, 3 in Switzerland, 2 in Belgium, 2 in Sweden, 1 in Italy, 9 in South Africa. At one of the German factories the first of these stills was received in January 1891 and is in use now; a large number of stills of the same kind has since been added.

At present the price of platinum is not very much less than that of gold (2600 marks against 3000 marks), so that a large

Delplace apparatus (p. 858), for 10–12 tons O.V. per day, weighing about 56 kil., will contain 52 kil. Pt and 4 kil. Au, and cost only about £80 more than if made of platinum entirely, whilst the annual saving in wear and tear (0·1 gram per ton of acid against 1 gram) amounts to £210.

Prentice stills (p. 856) can be constructed somewhat lighter, but the bottom is better formed of 0·2 mm. platinum and 0·2 mm. gold, the top of 0·25 mm. platinum and 0·05 mm. gold, if 97–98 per cent. acid is to be made, for which this system is specially well adapted.

The Heraeus platinum-gold combination may be regarded as the best kind for apparatus where *strong* and *pure* acid is concerned, both for entire stills and for pans covered with leaden hoods. The gold coating in the former case must be extended to the whole interior of the boiler, not merely to the bottom, as otherwise galvanic action sets in at the place where the acid touches both platinum and gold. The Heraeus composition is not adapted for impure acid, which forms crusts, as these necessarily cause damage to the gold, and as soon as any platinum is exposed the galvanic action sets in. Otherwise it is excellent.

It should be noticed that ordinary gold-plating, whether by electroplating or by the igneous method, does not fulfil the object of protecting the platinum, as practical tests have repeatedly proved. No doubt such gilding is always more or less porous, so that galvanic action with the sulphuric acid sooner or later sets in and injures the metal. This is not the case with the compact sheet of gold, rendered completely dense by rolling the Heraeus bars to the required thinness.

Crusts forming in Platinum Stills.

The iron salts contained in the chamber-acid in concentrating are precipitated as anhydrous *ferric sulphate*, which, being insoluble in strong sulphuric acid, partly attaches itself in white crusts to the vessel, partly remains suspended in the acid in shining flakes; the precipitate also contains a little lead. When it occurs in large quantities it may occasion stoppages of work and also make the acid more or less unsaleable. This especially happens when Glover-tower acid is employed for concentration. In order to remedy this, Gerstenhöfer suspended a large porcelain dish in the still by means of platinum wires, completely immersed in the acid, in which, owing to the boiling movement, all crusts &c. collect. The dish is taken out from time to time, which can be done very quickly (Bode, 'Beiträge,' 1872, pp. 50, 51). This arrangement seems to have been introduced in very few places, if at all. So much is certain, that hardly anywhere can Glover-tower acid be used for manufacturing "rectified oil of vitriol," and that the acid for this purpose is always obtained by a preliminary concentration of chamber-acid, which has not passed through the tower, in leaden pans, either by special fires or by steam-coils, or, more often and rationally, by the waste heat of the burner-gas, or by that of the stills themselves, as already frequently mentioned. In any one of these ways the acid is brought up to about 140° Tw. without having been in contact with the flue-dust from the pyrites-burners, which contaminates it with a comparatively large quantity of iron.

Even at factories where brimstone is burned the Glover-tower acid has not been found suitable for platinum stills, because it evidently dissolves too much iron (and alumina) from the "packing" of the tower.

But even with feeding-acid concentrated by bottom-heat only, the precipitation of salts in the platinum stills can be very rarely avoided, if the concentration proceeds beyond, say, 92 per cent. H_2SO_4. Wherever stronger acid is made, it becomes necessary to clean out the platinum stills from time to time, in order to avoid the formation of hard crusts, which would speedily ruin the still. This cleaning is effected by running the still as nearly dry as its form permits, and dissolving the salts by means of hot water or hot weak acid.

This operation has to be performed at various intervals, according to the circumstances of the case. Whilst at some works they have to do it every few days, they may elsewhere run on for several weeks or even months.

The following is the composition of crusts formed in platinum stills, as observed at a French works, according to private information:—

	Hard, stony crust.	Softer crust, impregnated with acid.
Fe_2O_3	33·60	23·00
SO_3	63·20	63·60
SiO_2	—	0·20

	Hard, stony crust.	Softer crust, impregnated with acid.
CaO	trace	1·10
$MgO+Na_2O$	trace	0·85
As_2O_5	trace	trace
$PbSO_4$	trace	trace
Se	trace	trace
Al_2O_3	trace	—

At Stolberg alumina is always found, sometimes exceeding the proportion of iron (1902).

An explosion on cleaning out a platinum still has been reported by Kuhlmann, jun. It occurred by running water upon some acid left in the still (the two strata evidently remaining separate) and starting the fire. At a certain point the two strata must have become suddenly mixed; and the explosion occurred through a violent evolution of vapour (Bull. Soc. Chem. vol. xxxiii. p. 50).

Concentration in Iron Vessels.

The great cost of platinum, and the liability of glass to breakage, together with the usually great expense for fuel in the latter case, have led to employing iron vessels for the concentration of sulphuric acid, as it is well known that iron resists strong acid, although it is so very rapidly dissolved by weaker acid.

For some time past cast-iron vessels have been in constant use for concentrating sulphuric acid up to the high strength required, especially for the manufacture of nitroglycerine and pyroxyline, say 98 per cent. H_2SO_4. This strength cannot be attained at all on a manufacturing scale in glass retorts, and in platinum vessels it causes an excessive wear and tear. Moreover the deposits formed in the latter, especially when re-working the spent acid of previous operations, are almost unbearable. There is, therefore, a special inducement for employing cast-iron vessels for this purpose, and this is frequently done. The principal condition is this, that cast-iron is not employed below a certain *strength* of acid. It would appear that this strength is best 93 or 94 per cent. H_2SO_4. Up to this point, then, the acid is brought in glass or in platinum; but beyond this cast-iron vessels may be employed, if certain precautions are observed. In some places they put in some sulphate of soda, which is believed to preserve the iron. In other places they employ long pans (about 10 feet, and 2 feet deep), covered with a leaden dome, in which the acid (not below 96 per cent.) is heated to 240°. At one end a stream of (heated?) air is blown in; at the other end the acid vapours escape by a lead tube into a lead condenser. The constant change of air allows of bringing the strength up to 98·5 per cent. At the end of the operation, when drawing off the concentrated acid, enough is left in to yield acid of not less than 96 per cent. when feeding with ordinary acid of 93 or 94 per cent. The iron is certainly acted upon, and deposits of anhydrous ferric sulphate are formed; there are also black particles (probably graphite) floating in the liquid. These particles, however, are removed without any special effort by the lead sulphate forming on the leaden cover and falling into the acid, as the sulphate carries down the black particles. (Comp. later on the sketch of such a pan as used for the recovery of acid from "acid-tar.")

In other places they employ pans with rounded corners, of 6 feet 6 inches by 3 feet 3 inches by 1 foot depth, with a rebate round the top, into which fits a shallow inverted pan provided with three necks (one for feeding, two for the acid vapours). The joints are made good with a mixture of asbestos and silicate-of-soda solution. Near the bottom there is an outlet-pipe for the acid. The pans are surrounded all over by fire-flues, which keep even the covers hot. Two such pans, placed terrace-wise, and weighing about 7 tons, inclusive of connections, are said to produce (from acid of 142° Tw.) 4 tons of 98 per cent. acid per day, with an expenditure of 25 or 27 per cent. of coals.

Figs. 397 & 398 show the cast-iron retorts usually employed in Germany. Each retort weighs about 2600 kil.; they last about four months. Francke (Fischer's Jahresb. 1898, p. 329) states that they concentrate up to 140 tons (?) acid from 93 to 97 or 98 per cent. H_2SO_4, each ton dissolving about 100 grams iron, with a consumption of 28 or 30 per cent. fuel.

Tate mentions pots, 9 feet wide and 6 feet deep, 2 in. thick, with cast-iron lids, weighing 11 or 12 tons, in which acid of spec. grav. 1·74 is concentrated within 28 or 30 hours to 96 per cent.; one such pot produces 12 tons of acid. It is allowed to settle and cool for 12 hours, so that one of these pots can be finished every two days. Coal used 2 cwt. per ton, wages 1*s.* per ton, wear and tear 3*s*. or 4*s*. per ton of finished acid. From time to time the mud consisting of iron salts must be cleaned out, and this represents 4 or 5 per cent. of acid lost. Such a pot costs £60, the lid (which lasts for 3 or 4 pots) £10, the setting £30. Each pot produces from 500 to 600 tons of acid, and is then worth £10 or £15 as old metal. The plant requires very little space and no expensive building. The dirtiest acid can be worked up which can hardly be worked by any other system, and the highest strength can be attained [but the acid will be very impure].

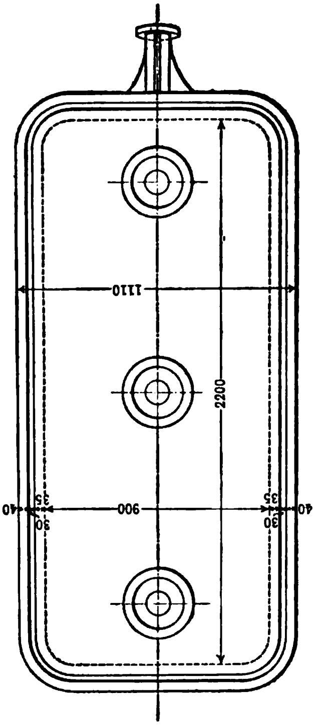


Fig. 397.

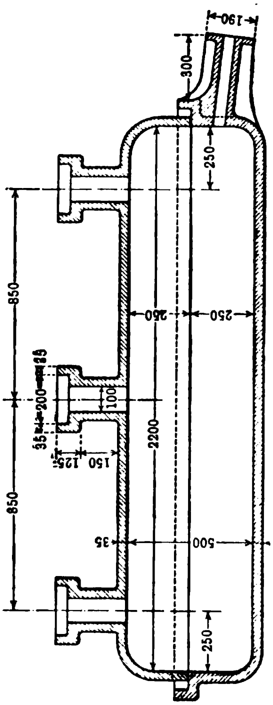


Fig. 398.

Scale 1 : 30.

In my report on a visit to America (Zsch. f. angew. Chem. 1894, p. 135) I have described the following plants :—In one place they concentrate the acid to 66° Bé. = 93·5 per cent. in platinum, above that, up to 98 per cent., in round cast-iron pans, 3 ft. wide and 2 in. thick, with double flange for a hydraulic joint, in which a water-cooled leaden hood dips. The hydraulic flanges are lined inside with lead, as they are filled with weak acid. Such a pan lasts two months.

At another place they employ a set of three pans: one is made of cast-iron, 4 ft. × 3 ft. area, and two of platinum, all three with lead hoods on the Faure-Kessler principle (comp. p. 866). In the platinum pans the acid rises to 65½° Bé., in the iron pan to 66° Bé. This acid is only used for purifying petroleum. All three pans are heated by heavy petroleum (spec. grav. 0·833, the residue from the manufacture of paraffin), injected by a steam-jet. The regularity and facility of this kind of heating compensate the excess of cost of coal. The flame, after heating the three pans, passes above the weaker acid contained in two lead pans, each 30 feet long and provided with an inner dry wall and a water-jacket as protection against being burnt through. The first lead pan receives chamber-acid of 53° Bé.; the second lead pan brings it up to 61° Bé., the second platinum pan to 65°·5, the iron pan to 66° Bé. Each set furnishes daily 500 carboys, or about 20 tons, with a consumption of 900 American gallons, or a little over 3 tons, of heavy petroleum, costing 2 cents per gallon, or 7·5 tons per 100 tons acid. The iron pans last three months.

At another place they have two platinum pans with lead hoods, the upper (weak) pan receiving the direct fire, combined with two specially fired iron retorts, constructed as described p. 882, viz., a bottom part, 8 ft. × 2 ft. section and 8 inches deep, connected by a flange and rust-joint with a similar shaped, but only 4 in. deep lid. The fire plays all round, first underneath the pan and then above it, in a 12-in. wide flue. The 6-in. vapour-pipe passes through this. The acid attains to 98 per cent., and is drawn off by means of an iron tap.

In a fourth factory, at Pinole, Cal., there is the following apparatus, for the drawings and description of which I am indebted to the superintendent, Mr. W. R. Quinan (now at the DeBeers Explosive Works, Cape Town). Fig. 399 (p. 887) shows the iron pan without cover, seen from above; fig. 400 is a sectional plan through A B, showing the steam-pipe and the outlet-pipe with mud-box; fig. 401 part of the longitudinal section through C D, showing the acid-inlet and the thickened bottom below it; fig. 402 a cross-section at right angles through the inlet. The pan is divided into three compartments by longitudinal partitions which leave openings at alternate ends of the pan, and thus compel the acid to travel in a zigzag manner. Corresponding to these channels, the pan-bottom is bulged outwards, in order to enlarge the heating-surface. The flat cover rests on a rebate formed on the upper edge of the pan, and is luted in this with a mixture of barytes and silicate of soda; it is held in its place by six castings, *a a*, wedged against corresponding lugs, *b b*, on the pan; these lugs also serve as bearers for the pan. The cast-iron vapour-pipe, *c*, 2½-inch bore, is connected by flanges and screw-clamps with a neck formed in the cover; the joint is made by an asbestos washer and the silicate-of-soda mixture. During work the pan-lid is tightly covered with asbestos waste, to protect it against cooling and the consequent action of the acid. The acid-inlet is not arranged in the cover, but in a cup, *e*, cast on to the pan; below this the pan-bottom is thickened, as this part is always strongly acted upon. The pans are 5 ft. 6 in. × 1 ft. 6 in. surface and 10 in. deep; the channels are 5 in. wide each, thickness of metal ⅝ in.

The acid-outlet is at the cast-iron neck, *f*, opposite which is a cleaning-hole in the pan-lid, with the cover, *d*, luted by silicate-of-soda cement. Neck *f* is joined to the cast-iron pipe, *g*, leading to the mud-box, *h*; from this a cast-iron pipe, *i*, again rises upwards, and is connected by a side-branch with the short platinum tube, *k*, which conveys the acid into a Johnson and Matthey's platinum cooler. By this arrangement the acid is obtained perfectly clear and free from mud.

This iron pan is connected with two Delplace platinum stills, 18 in. wide and 5 ft. long. The acid enters 62° Bé. strong from the lead pans into the first platinum still. The fire, on leaving the platinum stills, travels underneath seven lead pans; there are also lead pans on the eight sulphur-burners. This set of one cast-iron pan and two platinum stills, together with an auxiliary iron pan and platinum stills, supplies a set of chambers of 200,000 cubic feet.

The firing of both iron and platinum stills is performed by crude petroleum, sprayed by superheated steam. The introduction of this system, in lieu of a coal-fire, not merely saves labour, but it also increases the turn-out from 9 tons to 13½ tons of 96 per cent.

The duration of an iron pan is from four to eight months. They are rarely used up, but they crack in the places where thick crusts are formed, sometimes without apparent cause, probably in consequence of faults in casting. [Recently chilled cast-iron seems to have given great satisfaction.] Small holes sometimes forming at the inlet can be stopped up by silicate-of-soda cement. The vapour-pipe, *c*, leads to a condenser constructed of platinum and lead. Formerly it had to be protected against cooling and quick corrosion by a thick asbestos coating; but later on a cast-iron mixture was invented which lasts almost indefinitely even without such protection [probably chilled cast-iron].

During work a deposit is formed at the bottom, principally consisting of ferric sulphate, which is removed once a fortnight. The pan is emptied, the cover removed, the outlet *f* is closed, the pan is filled with water and heated to boiling. The crusts, which are sometimes ½ in. thick, are then chiselled off. Such crusts of course greatly diminish the heating efficiency. In the first channel, where the fresh acid enters, there is not much deposit—on the contrary, the iron is slightly acted upon ; and the ferrous sulphate, together with that issuing from the chambers in large quantities (comp. below), is deposited in the second and third channels. A little mud is always carried along by the acid, but is deposited in box *h*.

The acid made by this apparatus, remarkable to say, contains less iron than that formerly concentrated to 96 per cent. in platinum stills at the same works. No doubt this is caused by the fact that they now bring up the acid to 97 or 98 per cent. But it is possible to turn out 95 per cent. or even 94 per cent. acid in this apparatus.

As to the consumption of fuel, more is used with iron pans than with platinum stills. Formerly the consumption of coal for making 96 per cent. acid in platinum stills, inclusive of chamber-steam, was 22 per cent. of the acid; now, for making 97 per cent. acid in iron pans it is the equivalent of 28 to 30 per cent. of coal (used in the shape of petroleum).

At the same works they treat a large quantity of *waste acid from the manufacture of nitro-glycerine.* This after denitration yields acid of 53° Bé., which was formerly concentrated in special top-fired lead pans, and subsequently in the above-described combined iron and platinum stills. But as the mixed acids are sent backwards and forwards in sheet-iron glycerine drums and

Fig. 399.

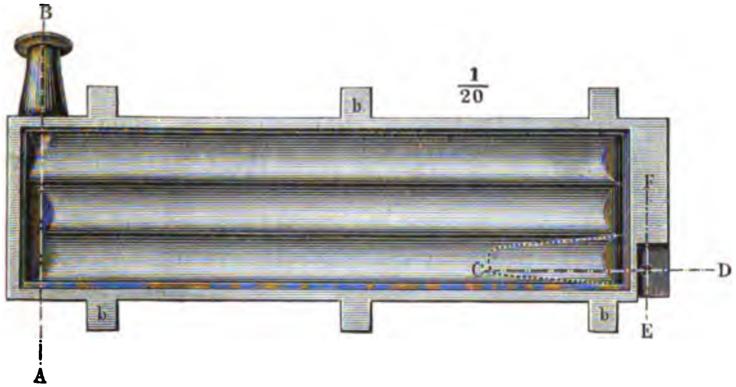


Fig. 400.

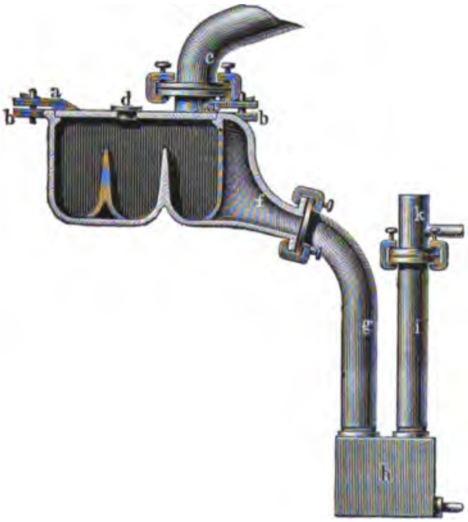


Fig. 401.

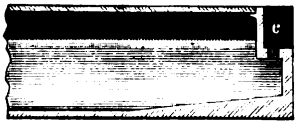
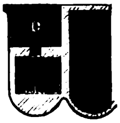


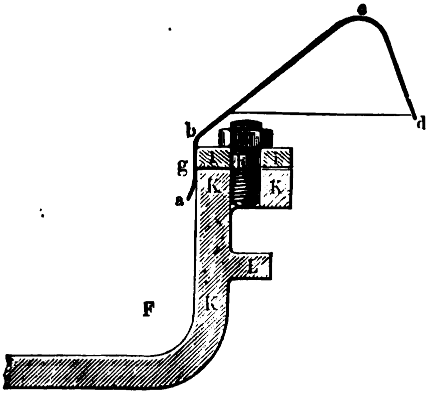
Fig. 402.



take up much iron from these, the denitrated acid is now run into the chambers, where much of the mud is deposited, and the chamber-acid is then treated as above. Such acid could not possibly be concentrated in platinum stills alone, on account of the crusts.

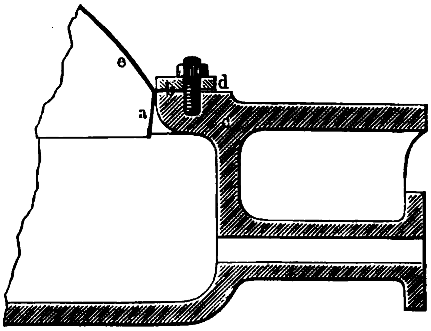
Scheurer-Kestner (Bull. Soc. Ind. Mulhouse, 1892, p. 348) employs the following connection between the iron pan and a platinum lute for receiving a Faure and Kessler hood (fig. 403). F is the cast-iron pan, resting on the brickwork by means of the flange L. *a, b, c, d* is the platinum rim, to which is soldered a flange *g, h,* held between the flange K, cast on the pan F, and a loose iron flange *i i,* the joint being made with asbestos or gypsum pipeclay and secured by screw-bolts. The apron *g, a,* forming part of the platinum rim, protects the cast-iron from the drops of weak acid falling fron the top. A cast-iron pan supplying 5 tons of acid in 24 hours weighs 5 cwt.: it yields on the average 12·7 grams iron to 100 kilograms acid concentrated from 92·5 to 96 per cent. The platinum pan, in which the previous concentration to 92·5 per cent. is effected, suffers very little indeed. The concentration in iron is not suitable below 95 per cent. or much above this point.

Fig. 403.



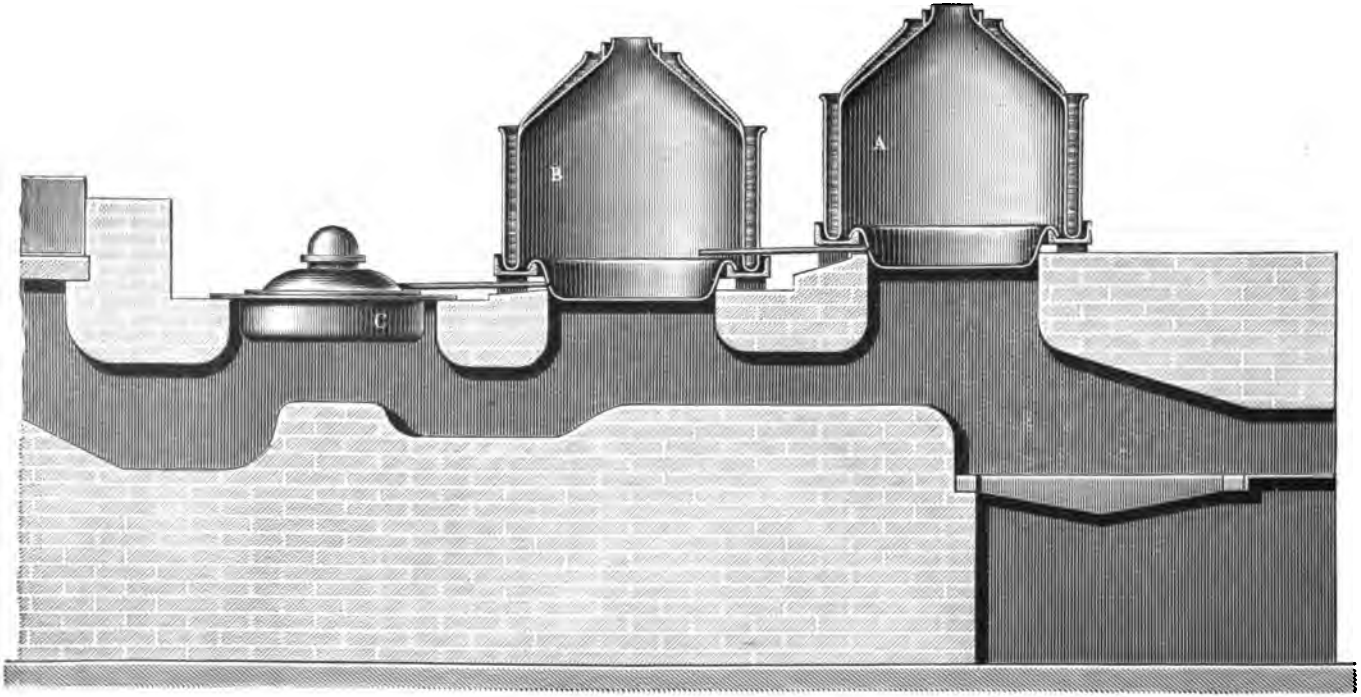
For this reason Scheurer-Kestner prefers the following *combination of a cast-iron pan with platinum dome* (Germ. pat. 61,331; Bull. Soc. Ind. Mulhouse, 1892, p. 320). Fig. 404 again shows the arrangement of protecting the iron from drops of weak acid by the platinum apron *a,* and of forming the joint by means of the platinum flange *b*, held between the iron flanges *c* and *d*. But here the platinum continues into a real hood *e*, closed at top in the ordinary manner. The iron pan C, which weighs 250 kil., must be entirely surrounded by the fire, as shown in fig. 405. The platinum dome weighs from 8 to 8·5 kil., and the preceding two platinum dishes B and A, provided with Faure and Kessler hoods, weigh 9 kil. each, the connection-tubes about 2 kil. The fire plays first under the weak platinum pan, then under the stronger platinum pan, at last under the iron pan. Such an apparatus furnishes 4½ tons of 95 per cent. acid in 24 hours, with less than 0·15 gram platinum lost for each ton of acid; and the concentration can be easily driven to 97·5 per cent.

Fig. 404.



The Clayton Aniline Co. (E. P. 11,544, 1898) employs cast iron pans in such a manner that the acid, of any desired strength, is run on to the centre of the surface of heated acid containing not below 90 or 93 per cent. H_2SO_4, at the same time withdrawing so much strong acid from the bottom of the vessel that the level remains nearly constant. This system is shown in fig. 406. Pan *a* has an overflow pipe *b*, starting near the bottom of the pan at *c* and delivering the acid at *d* at a suitable level. On flange *e* the cover *f* is fixed by screw-clamps *g g*, with suitable cement. Through neck *h* the fresh acid is introduced. In neck *k* a pipe *l* is fixed, through which the vapours escape which are condensed by means of chamber *m* and cooling-pipes *n n*. Through another neck a thermometer is introduced into the pan. For a start pan *a* is charged with acid of 90 to 93 per cent. which is heated to boiling, whereupon fresh diluted acid is run into the pan in

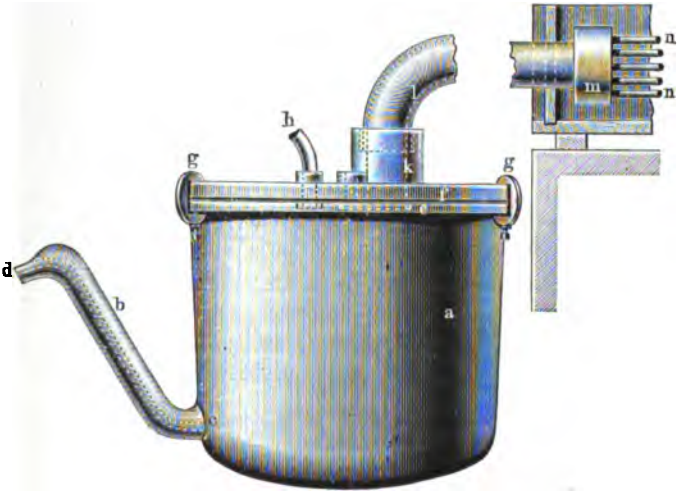
Fig. 405.



suitable proportions, striking the acid in *a* about the central part. The supply is regulated in such a manner that the level remains practically constant, the strong acid running off at *d* and the vapours escaping at *l*. (An altogether similar process is described in Gridley's U.S. P. No. 265,495, of 1882.)

This apparatus has since been combined with another, intended to deal with the acid fumes, to be described below.

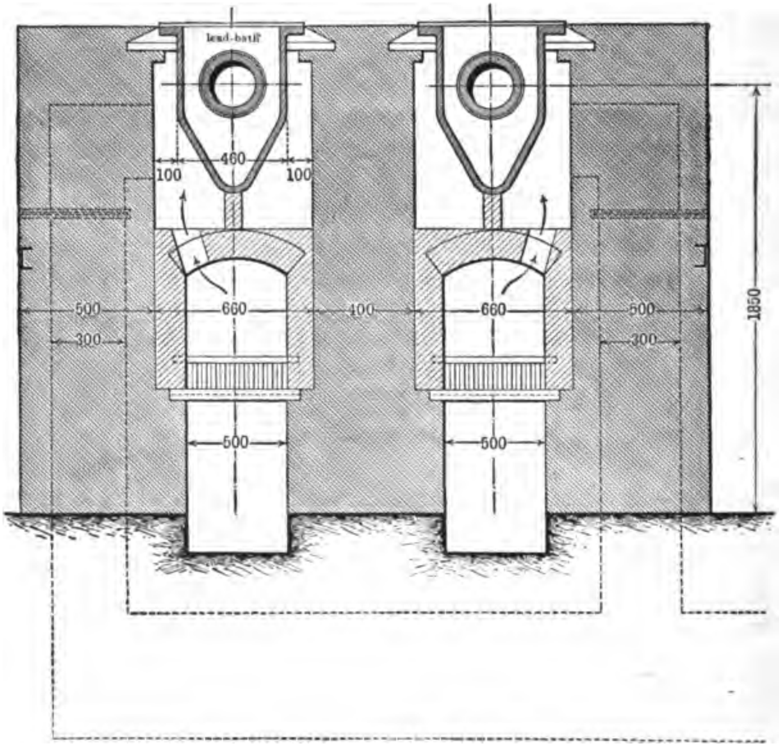
Fig. 406.



G. Krell, of Bruchhausen near Küsten in Westphalia, has constructed an apparatus, consisting of a cast-iron pipe heated in a bath of molten lead, the ends being water-cooled so that the solid lead forms a tight joint against the molten portion. Figs. 407–409 show this system with all details (Engl. pat. 18,727, 1894). One such pipe, costing £4 to £4 10*s*., yields from 300 to 500 tons strong sulphuric acid, according to the strength of the feeding-acid, with one man per shift. The cleaning can be mostly performed without any stoppage of work; once a week, or in two or three weeks, a thorough cleaning must be effected, which involves a stoppage of half a shift. An apparatus for turning out 5 tons commercial O.V. (92 to 93 per cent.) requires a ground space of 120 square feet, including cooling-apparatus, and costs £150, or inclusive of all auxiliary apparatus, brickwork, &c.,

£250, to which must be added £250 for the license, plans, and instructions. For acid of 97 per cent. H_2SO_4 iron pipes are employed at an additional cost of £100. This plan works very well for concentrating Glover acid or wash-acids from nitroglycerine &c. It has been at work for some years in several factories in Germany and Poland. M. Liebig (Zschr. angew. Ch. 1900, p. 184) speaks very well of it.

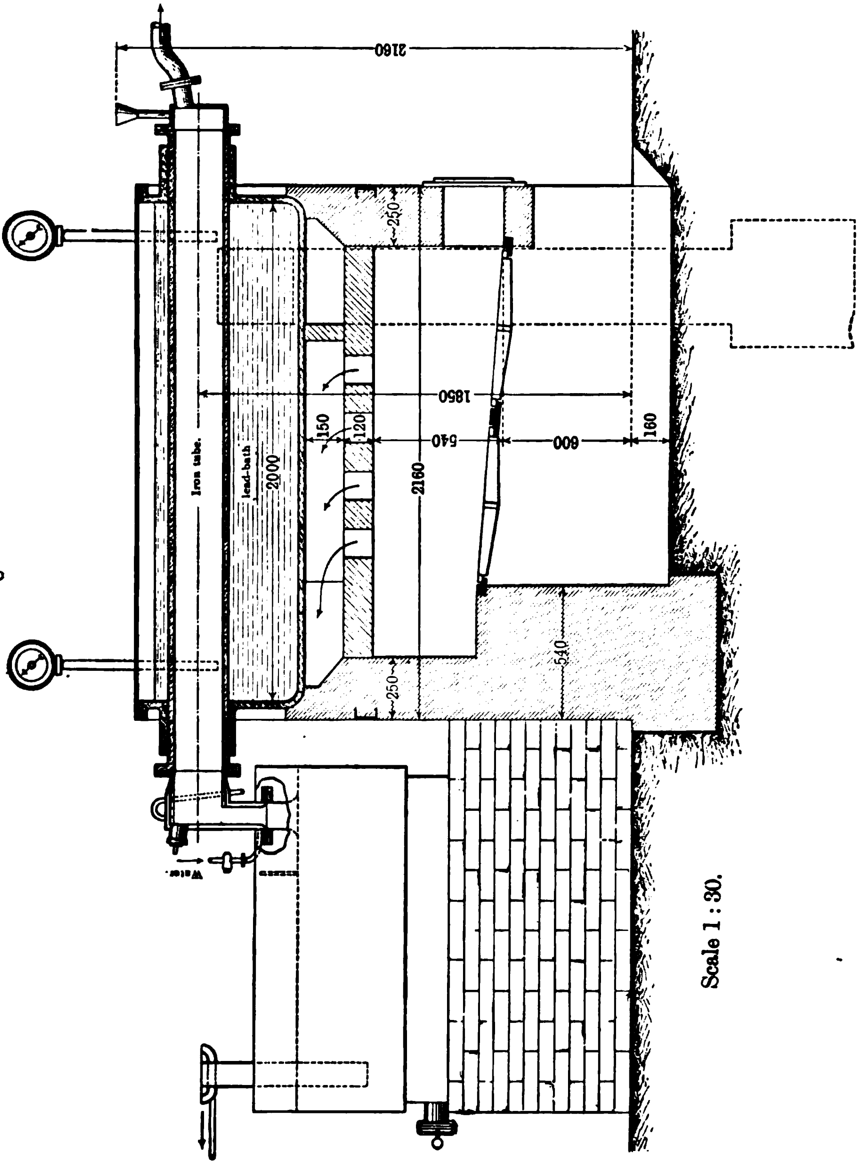
Fig. 407.



A new plan was proposed by Hartmann (Engl. pat. 2839, 1879). The acid is to be saturated with iron salts, which are again separated on concentration, and are intended to protect the iron of the pan itself.

The following process is intended to combine concentration of sulphuric acid with purification from iron and arsenic. Menzies (E. P. No. 3230, 1883) asserts that sulphuric acid of the highest concentration can contain but traces of iron and arsenic in

Fig. 408.



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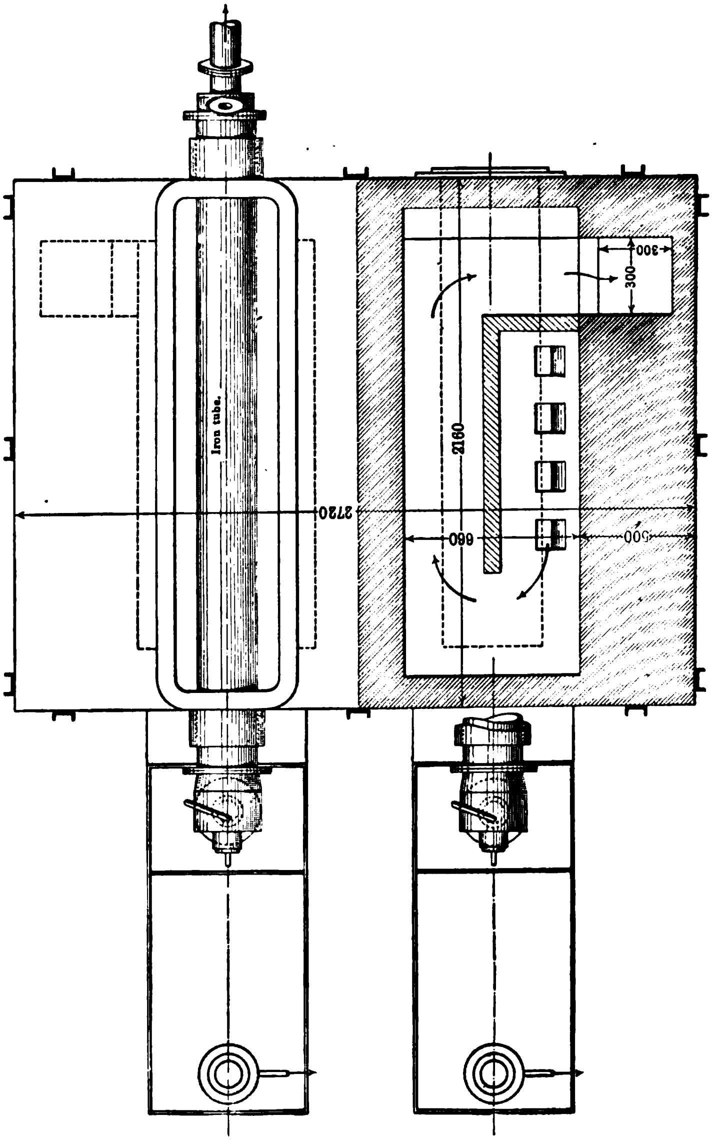


Fig. 409.

solution, provided the latter be present as arsenic acid. He adds some nitric acid, in order to oxidize any As_2O_3 to As_2O_5, and boils the acid in a cast-iron pan, the bottom of which is not exposed to the fire, until the strength of the acid distilling over is about 142° Tw. The fire is now drawn, the acid is allowed to settle, and ⅔ or ¾ of the clear acid is withdrawn. This acid is colourless and free from Fe and As [?], and 3 or 4 per cent. stronger than ordinary "rectified O.V." Fresh oxidized acid is run into that which has remained in the pan, in such a way that the strength never falls below that at which the iron is acted upon by the acid. According to analyses quoted in the 20th Official Alkali Report (for 1883), p. 45, the quantity of iron found in the concentrated acid, calculated as Fe, is only from 0·006 to 0·022 per cent.; that of As, 0·013 to 0·015 per cent.; that of N_2O_3, 0·011 to 0·024 per cent. The precipitate at the bottom of the still contains 50 SO_3, 20 As_2O_5, 28·2 Fe_2O_5, 1·8 insoluble, &c.

These figures show that the removal of arsenic by Menzies's process is nothing like complete. Menzies believes that acid of 58° Baumé does not act (in the heat) upon cast-iron; but that is a great mistake, and in practice he must have dissolved a large quantity of iron which no doubt in the latter stage of the process would be again separated in the shape of anhydrous ferric sulphate.

In the 28th Alkali Report, p. 55, Graham's process is mentioned, in which the concentration takes place in a series of cast-iron dishes. It was found that hot sulphuric acid, in thin layers, in contact with cast-iron, tends to dissociate into SO_3 and H_2O, so that from a certain point the acid becomes all the weaker the longer and more strongly it has been heated. The dissociation is evidently caused by the superheating of the iron, which becomes much hotter than the platinum. This observation proves the advantage, formerly pointed out, of causing the flame to travel in the same direction as the acid, so that the strongest acid is not in contact with the hottest part of the flame.

Fisher, Hall, and Moore (E. P. 27,376, 1898) let the acid run through a long cast-iron pipe heated outside, to produce continuous concentration.

The 38th Alkali Report, p. 18, mentions a process of American origin, by which sulphuric acid is rectified continuously in a cast-iron vessel, all air being excluded from the space above the liquid acid. In this case there is no difficulty in condensing all the SO_3; very little SO_2 is formed and the gases escaping are not in the vesicular condition rendering condensation so difficult and imperfect in other processes. The process had not been at work sufficiently long to test all these claims.

P. Kestner (G. P. 121,339) concentrates the acid by heating it in a perpendicular iron tube, in which it is raised to a higher level by the gas-bubbles.

Those apparatus where cast-iron vessels are used in connection with a *vacuum* process will be mentioned later on.

Concentration of Sulphuric Acid in Wrought-iron Vessels.—Tate (Journ. Soc. Chem. Ind. 1894, p. 208) gives particulars of an old tar-still, made of ⅜-inch plate, 6 ft. wide and 4 ft. high, in which for several years past a mixture of sulphuric and nitric acid had been concentrated from spec. grav. 1·75 to 1·838, with recovery of the nitric acid. [Perhaps the use to which this vessel had previously been applied had deposited a protective, carbonaceous coating.]

It cannot be denied that under the most favourable circumstances the concentration of sulphuric acid in iron pans is connected with many troubles; and this has lead to a number of firms giving them up again and going in for platinum stills, in spite of their very high price and the great wear and tear when driving the concentration to 98 per cent. acid.

Mr. G. E. Davis informs me that at their chlorine-works they rectified over 40 tons O.V. weekly for over ten months in iron, at a slightly cheaper cost than in glass, but the acid was not so good in colour, although it deposited all iron on cooling.

We have previously (*supra*, p. 203) discussed the *action of sulphuric acid on cast-iron,* and we subjoin here further notes on this subject.

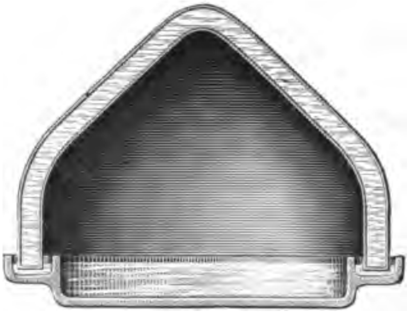
Föhr (Fischer's Jahresb. 1886, p. 295) points out that iron, in order to resist acids, ought to possess much chemically combined and little graphitoidal carbon, whilst precisely the opposite holds good with reference to resistance against alkali, as in caustic-pots and the like. In the former case the iron ought to contain much manganese and little silicon, in the latter little manganese and much silicon. Fusing alkalies dissolve combined carbon and manganese, but very little graphite or silicon [?]. A mixture which makes good decomposing-pans (or acid concentrating-pans) would make bad caustic-pots, and *vice versâ.*

Recovery of strong Sulphuric Acid from Waste Acids (Acid-tar, Sludge-acid).

For this purpose nearly always iron pans, usually preceded by lead pans, are employed, as such dirty acids generally form crusts which speedily destroy platinum pans. The unavoidable contamination of the acid with iron is also no great drawback in this case, as the recovered acid is again used for the treatment of mineral oils, &c.

The following process serves for the concentration of acid recovered from the "acid-tar" or "sludge-acid" of petroleum refineries. This acid-tar is first diluted with water, whereupon most of the tar is separated and skimmed off (U.S. P. of Fales, No. 97,182, of 1867). The acid liquor is now concentrated in leaden pans, first by bottom heat and then by top heat, up to a strength of 64° Baumé (American hydrometer). The last concentration takes place in cast-iron pans with leaden hoods. The pans, two of which work together terrace-wise, are 2 × 4 feet wide and 6 inches deep; they have a rim shaped for a hydraulic lute, lined with lead, into which dips a double-walled, roof-shaped, leaden hood, through which water is kept running, on the principle of Faure and Kessler's stills (p. 866 *et seq.*). All the joints are made with asbestos cement. The principle of this apparatus is shown in the sketch, fig. 410.

Fig. 410.



Ostrejko (Chem. Zeit. 1902, Rep. p. 360) describes the recovery of sulphuric acid from acid-tar by the well-known process of diluting to 32° B., separating the tar, and concentrating to 60° B. In order to complete the separation, the acid is again diluted with chamber-acid or water and boiled down. The removal of the tar is promoted by a certain description of carbon invented by the author of that communication; 1 per cent. of this is said to convert the acid into a colourless product.

U. Wedge (Journ. Soc. Chem. Ind. 1899, p. 345) describes the usual process of working up the "sludge-acid" from the petroleum refineries. As it comes from these it contains about 45 per cent. of oil. Most of this is separated by diluting the acid to 35° Baumé; it is called "acid-oil" and is utilized as fuel. The weak acid, separated from it, still contains 1·2 per cent. oil. It is heated in a shallow, hooded lead pan by means of a light steam-coil to 110° C., in which process a very slight quantity of SO_2 is formed. The acid now enters a series of three shallow lead pans, 6 × 45 feet, 12 in. deep, covered with brick arches, where it is treated with surface-fire ("weak-acid pans"). Here it gets up to 56° B. and a temperature of 166° C., with some loss of SO_2 and SO_3 (the gases showed 1·24 grain SO_2 and 0·92 grain SO_3 per cubic foot). Now the acid enters a series of two lead pans of the same size as the above and at last two iron pans 3 × 7 feet, 9 in. deep. The lead pans are also housed in brick and heated by surface-fire. From these ("strong-acid pans") the acid issues with a temperature of 230° C. and shows 66° B.=92½ per cent. acidity. The gases from these pans showed 28·7 grains SO_2 and 4·9 grains SO_3 per cubic foot. There was a total loss of 25 per cent. of the acid, 91 per cent. of which occurs in concentrating from 56° to 66° B., 86 per cent. being caused by the action of the oil on the sulphuric acid forming SO_2, which cannot be recovered in consequence of the style of heating by surface-firing. Calculation shows that 1 lb. of the hydrocarbon dissolved in the oil will destroy 20·88 lbs. acid of 92½ per cent.

The treatment of sludge-acids in iron vacuum-retorts will be described later on.

Hartmann (Chem. Zeit. 1899, p. 147) concentrates waste acid from nitrating processes up to 61° B. (spec. gr. 1·732) in six lead pans. The acid, at a temperature of 145° or 150°, then passes through a small "preliminary" cast-iron pan, provided with a leaden hood and a chimney for carrying away the vapours which contain very little acid. Now, 180° hot, and of spec. grav. 1·785 to 1·796, it runs into two cast-iron pans with cast-iron covers, one placed higher than the other, and runs away at a strength of 97 or 98 per cent. H_2SO_4. Each of the latter has its own fire, as well as the "preliminary" pan, the waste heat of all heating the lead pans. For the production of 5½ to 6 tons strong acid in 24 hours, the preliminary pan weighs about 24 cwt., the two covered pans with appurtenances about 7½ tons. The consumption of coal is 20 per cent. The small pan lasts 3 or 4 months, the upper one of the large pans 6 to 9 months, the lower one 12 months or more. The castings should be made of hard metal and without flaws, and the two large pans must be entirely surrounded by the fire. The wear and tear of these castings represent 2*s.* per ton of strong acid. The cost of the whole plant, including all auxiliary apparatus, is about £750. It should be mentioned that *platinum* retorts would suffer enormously if waste acid was to be brought up to 97 or 98 per cent.

Benker has applied his porcelain apparatus (p. 850) also to the recovery of waste acids. In the case of acid-tar from refining petroleum there is a loss of about 40 per cent.; the acid is coloured black owing to the formation of graphite, but furnishes water-white petroleum. The recovered acids from nitroglycerine or nitrocellulose are yellowish, but perfectly fit for being used over again.

Waring and Breckenbridge (U.S. P. 643,578, of 1900) purify sludge-acid by heating with about 4 per cent. sodium nitrate at a temperature of 15° to 82° C.; 1 per cent. $NaNO_3$ suffices for removing offensive odours.

Friedland and Ljubobarski (Russ. pat. 6631) dilute the acid-tar, skim off the tar, allow to settle, and submit the clear liquid, brought to 50° B., to the electric current, which oxidizes the carbonaceous matter to CO_2.

Cast-iron Pans protected by Enamel or otherwise.

It might be thought that *enamelled* cast-iron would be more suitable for this purpose than ordinary cast-iron. In fact Roder (Dingl. Journ. cxi. p. 397) proposed enamelled cast-iron boilers, and indicated a special kind of enamel for them: 1 part of powdered burnt alum, 4 parts of red-lead, and 2 parts of pure silica are to be melted together; the fluxed mass is to be cooled in water, dried, powdered, and 15 parts of it intimately mixed with 20 parts of pure silica and 3 parts of tin oxide. The whole is ground up with spirit of turpentine, laid with a soft hair-brush on the smoothly turned inner surface of the boiler; and this is repeated three or four times, each coat being allowed to dry first. The enamel is then fixed by fusing on as usual. But even the best enamel will certainly resist only a very short time the boiling vitriol and the uneven expansion and contraction of metal and enamel at the very greatly differing temperatures which occur, and his proposal has had no practical success.

Wolters (G. P. 15,639) states that by heating a mixture of alkaline pyrosulphate with concentrated sulphuric acid in iron vessels a crust of iron sulphide is formed which protects the iron during distillation, so long as the pyrosulphate is left in the vessel.

Tate (Journ. Soc. Chem. Ind. 1894, p. 208) mentions an apparatus constructed by West in 1883 on the continuous system, with an enamel or porcelain lining; nothing is known as to its success.

Dyson (Engl. pat. 17,699, 1893, & 27,769, 1896) has made a cascade-apparatus, consisting of iron pans lined with a special enamel, connected by U-shaped siphons, which carry the acid from the bottom of each vessel into the upper part of the next. A set of 18 pans produces 21 tons of strong acid per week. This apparatus is to cost £250, and to require 6 cwt. of coke per ton of acid. Some more details are given in Chem. Trade Journ. xvii. p. 339. Chamber-acid of 100° Tw. is employed, and 100 tons acid of 168° Tw. is produced in one apparatus in 43 days, with a consumption of 23¼ tons of gas-coke; the wages are £19 9*s*. 7*d*., or 3*s*. 10½*d*. per ton, which would be greatly reduced if the same men could look after two plants. In 1902 several plants on this system were in operation in England.

Seckendorff (Wagner's Jahresb. 1855, p. 56) proposed to concentrate the acid in flat-bottomed iron retorts completely surrounded by fire. The retorts are to be filled with lead sulphate, sand, or gypsum; chamber-acid is to be run in till a paste is formed, and the retorts are then to be heated. The watery vapour first appearing is conducted into the chambers; the concentrated acid coming after this is to be collected in glass or stoneware vessels, and is said to be very pure, free from iron, and as concentrated as that from platinum; nor is the iron retort said to be acted upon very strongly. Probably this plan has never been actually tried at all.

J. Grindley (Amer. pat. 265,495) recommends cast-iron pans, protected at the top by an asbestos cement against the action of the acid. The pan is filled up to the proper level with acid of 66° B., and is fed in such a manner that the concentration never sinks below 65° B., in which case the pan is not acted upon.

[This strength, equal to less than 90 per cent. H_2SO_4, is much too low to prevent action on the iron. The corresponding English patent No. 4709, 1882, has not been proceeded with.]

Flanagan (E. P. 3530, 1901) employs enamelled cast-iron pans, with water-cooled leaden hoods, placed at different elevations. There seems to be no new principle whatever in this invention.

Concentration of Sulphuric Acid by hot Gases.

Stoddart (Chem. News, xxiii. p. 167) proposed *to force a current of cold air* into sulphuric acid heated in a lead pan; acid of 140° Tw. is stated to be obtainable in this way if the temperature be 150° C., and the strongest oil of vitriol at a temperature of 260° C. This plan, if ever carried out on a large scale, was no doubt very soon given up again. There is no reason why a current of air should not do much more harm by cooling the acid than it can do good by carrying away the vapour more quickly, the latter being done much better by top fire, where there is also no danger of splashing. It is well known that lead pans would not very long stand a temperature of 260° C.

Galletly (Chem. News, xxiv. p. 106), who had applied the same principle independently of Stoddart, only worked on a laboratory scale; he admits that on a large scale the process did not succeed; nor need we wonder at this, since both he and Stoddart applied *cold* air.

Success in this direction could only be expected from the application of *hot* air, which seems to have been first tried by Gossage in 1850.

Gossage's apparatus is fully described and illustrated in our second edition, p. 735 *et seq.* It consists of a double-shelled lead tower, with an air-space between the two shells; the tower is packed with pebbles, over which the dilute acid trickles down, and is concentrated by a current of air, heated up in a parallel series of iron pipes, and passing through the tower in a downward direction. This apparatus has never come into use; its faults are the following:—The air must be made nearly red-hot, and thus the upper lead pipe always melts; the air, charged with vapour, travels in the same direction as the acid, and therefore again gives up its water to the latter as it becomes more highly concentrated; all acid escaping along with the hot air is lost in the chimney. Although some of these faults might be avoided by changing the details of construction, the apparatus seems never to have been employed in practical work.

Gossage's plan has been re-invented by Cotelle, without any additions (Chemical News, xx. p. 107).

S. T. McDougall (Amer. pat. 289,293) employs a tower, heated from without, filled with dishes, over which the acid flows down whilst heated air ascends in the tower (comp. Nobel's patent, p. 855).

Similar in principle, although very different in detail, is the hot-air concentrator patented by the International Vacuum-Eismaschinen-Verein (G. P. 33,172). It does not seem to have answered, as the same firm a year later took out a patent (No. 38,015) for a totally different apparatus, working with steam, as already mentioned on p. 832.

Finch (E. P. 2207, 1886) combines an evaporating-furnace with two towers filled with refractory material. The furnace-bed is formed by a lead tank, lined with sheet asbestos, and upon this with silica bricks. The roof of the furnace is formed of silica bricks and covered outside with lead. The weak acid first passes through the towers and then into the furnace; the fire-gases make the opposite way. [It is very unlikely that an apparatus such as described will be able to stand the wear and tear of the process for any length of time.]

Fontenille (Germ. pat. 37,713) causes hot air to issue by means of many holes from a pipe at the bottom of a vessel filled with sulphuric acid; the vapours pass in a zigzag manner over several plates, over which fresh acid is running down. [It is not stated what material the vessel is to consist of. This proposal is not sufficiently worked out to be practical, and the utilization of the hot air will hardly be very efficient.]

Gridley (U.S. P. No. 240,248) applies strong heat to the under surface of a thin body of dilute acid, and at the same time a blast of superheated steam or hot air to the upper surface, removing the vapours as they rise.

Falding (Engl. pat. 17,602, 1893; U.S. P. 541,041) constructs the pyrites-kilns with hollow walls, by which the air passing through is heated, and can at will be introduced below the grates (comp. p. 307). The hot burner-gases are used for concentrating sulphuric acid, by passing them first into a small tower, consisting of specially acid- and heat-proof material (viz. Volvic lava of best quality), surrounded by a somewhat distant lead shell and packed with quartz. This tower is placed between the burners and the Glover tower, and receives the acid coming from the latter, which is here concentrated to 66° Bé. The gases pass first into this intermediate tower, then into the Glover tower. Of course this acid is not pure. For pure acid the concentration in the first tower is brought only to 71·08 per cent. SO_3; it is then run through a platinum tube into iron stills, as shown p. 882, where very pure acid up to 76·33 per cent. SO_3 distils over, while impure acid of 79·18 to 80·00 per cent. SO_3 (97 to 98 per cent. H_2SO_4) remains in the still, together with a mud of ferric sulphate and arsenic.—Falding thus applies the Glover tower to concentrate sulphuric acid to higher strengths than is done in the ordinary Glover tower, by constructing it with special care; but although he succeeded in getting acid up to about 90 per cent. H_2SO_4, his plan has not found much application (comp. Quinan's plan, *infrà*, p. 912).

The only hot-air process which has been thoroughly worked out, and is now introduced in many factories, is that of L. Kessler (Engl. pat. 19,215, 1891, and 26,169, 1898). I am indebted for the following particulars, as well as the drawings, figs. 411 to 413 (pp. 905, 906) to the inventor, and I have myself seen the process in operation at Clermont-Ferrand and in several other places.

The task in question requires several conditions to be fulfilled. The current of hot air must be brought into contact with a sufficiently large surface of liquid to immediately reduce its temperature to a great extent. The air must thus become completely saturated with steam and acid-vapour. The apparatus must not merely resist the action of the hot air and hot acid, but it must be constructed in such a manner that the inevitably formed deposits and crusts do not give any trouble. Under these circumstances the acid can be concentrated far below its boiling-point. In order to produce acid of 95 per cent., boiling at 284° C., the temperature need not exceed 170° or 180°; for the most highly concentrated acid, boiling at 320°, 200° to 230° is sufficient.

In order to denote both functions of this part of the apparatus visible at *c*, Kessler calls it a "saturex," because it saturates the fire-gases with acid-vapours, and it quenches the greatest part of their heat. The gases enter the "saturex" at 300° to 450° C., and leave it at 150°. The acid-vapour contained therein is kept back in the "recuperator" mounted above the "saturex." This part of the apparatus exactly resembles the dephlegmating columns employed in the rectification of spirit of wine. It is fed with chamber-acid, previously employed for cooling the hot, strong acid issuing from the "saturex." This acid is divided over the numerous holes of the top plate, and gradually descends on to the four lower plates of the recuperator. In doing so it meets the hot air and vapour issuing from the saturex, and drawn through the liquid acid by applying suction at the end. In the recuperator the temperature sinks to 85° C.: this causes nearly the whole of the acid-vapour to condense, while the steam is not condensed, nor is there much fresh steam formed here. This is important, since any concentration of the acid in this place would cause deposits which would soon obstruct the holes in the plates.

Although the gases escaping from the recuperator contain next to no real *acid-vapour,* they contain some acid in the shape of *mist,* as well as some vapour of sulphuric anhydride. This mist is retained by two boxes filled with dry coke in pieces about the size of a pea (comp. *infrà,* p. 908); a little water condensing here converts the SO_3 into SO_4H_2. The weak acid thus formed may be passed through the recuperator. The gases now issue into the air, moderately warm and perfectly free from acid, but charged with all the steam driven out of the chamber-acid. The distilling acid is thus completely condensed without the necessity of employing any cooling-water.

Figs. 411 and 412 show the apparatus. Fig. 411 is a longitudinal section through line J K; fig. 412 a cross section through the "saturex" according to line *m n*; fig. 413 an enlarged section through some of the plates of the "recuperator." *a* is the fire-place, here shown as a simple grating, but in reality a gas-producer, with gas-coke as fuel. The fire-gases pass through a cast-iron pipe *b,* flattened below so as to cover the whole breadth of the saturex *c.* This is a trough, composed of acid-proof stone slabs, surrounded by a thick lead jacket and placed upon an open foundation. The stone must resist hot acid and hot gases, *e. g.* Volvic lava; but even if it were somewhat porous, the lead jacket would retain any acid penetrating through the stone, a little sand being put between the stone and lead. The latter in actual work feels only moderately hot. Between the bottom and the cover of the "saturex" there are several thin partitions, *d d,* which force the fire-gases, entering at 300° or 450° C., to circulate over the

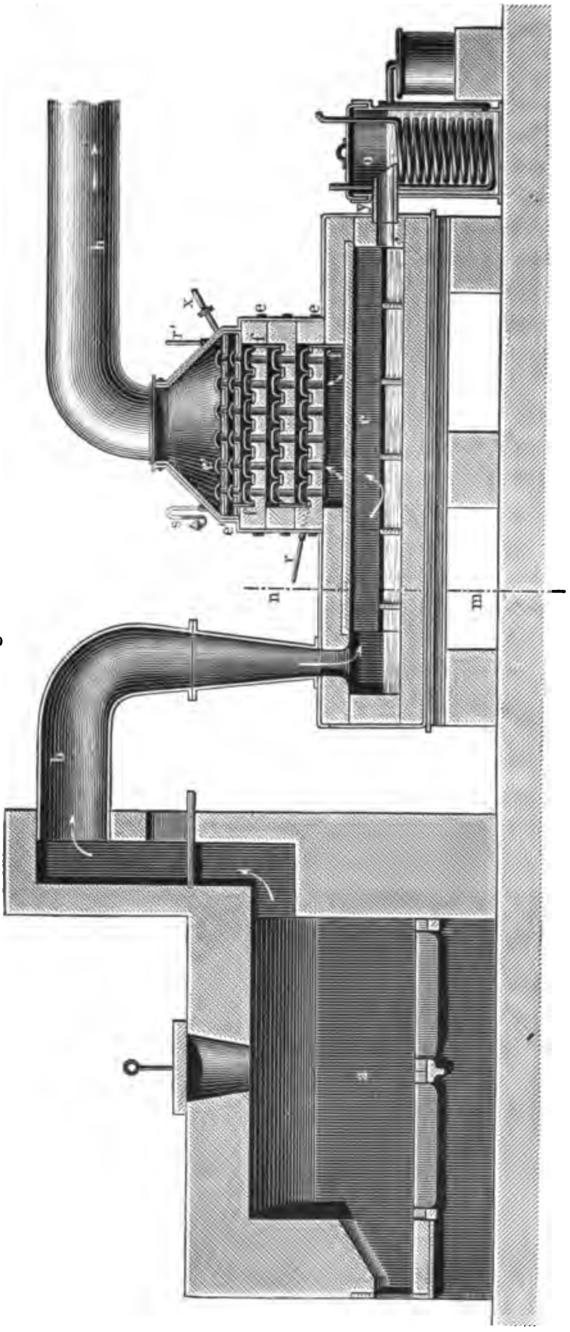


Fig. 411.

Fig. 412.

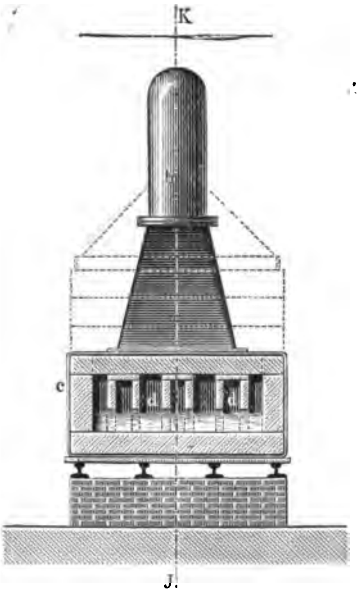
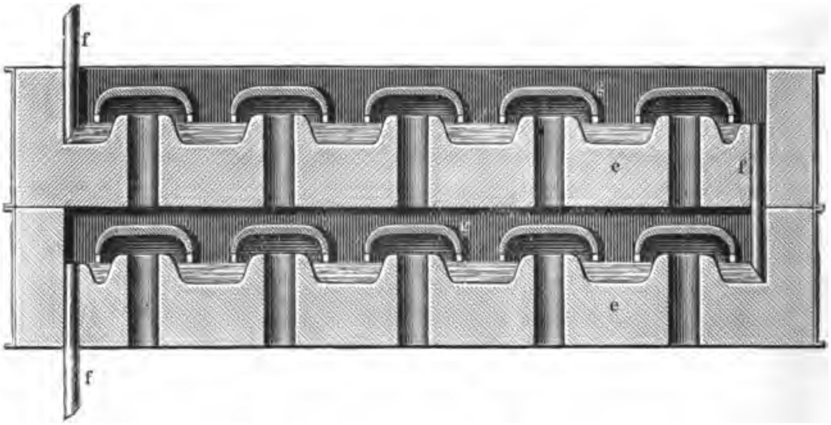


Fig. 413.



level of the acid in *c*; when passing from one of these flues to another they are forced almost through the acid itself, and are therefore quickly brought down to 150° C.; the acid just as quickly gives up its water and even some acid-vapour, and continuously runs off at *y* in the concentrated state into a cooler *o*.

The "recuperator" contains three lower stone plates, *e e e*, and two upper lead plates, c' c', all of them arranged as shown in fig. 413. Each plate has 100 holes with somewhat raised margins, so that a thin layer of acid remains standing upon it. The cups, *g*, *g*, made of porcelain with jagged edges, produce a hydraulic seal or at least a great resistance to the passage of the air. The acid arrives as chamber-acid of spec. grav. 1·58 through pipe *x*, and by the overflows *f f* it runs from one plate to another, finally into the saturex. The gases coming from the latter are by an injector drawn through the holes, from underneath the porcelain cups *g g*, and are thus brought into intimate contact with the liquid. r r' are thermometers, which serve for regulating the work: the lower, *r*, ought to show about 150° C.; the upper, r', about 85° C. *s* is a pressure-gauge for the aspiration; *h* the pipe leading to the coke-boxes. The concentration can be driven to 98 per cent. H_2SO_4, and the most impure Glover acid can be used, because in the recuperator there is no evaporation, and therefore no formation of crusts; and in the saturex the latter can collect for a long time without interfering with the process, and can be removed through cleaning-holes with hardly any interruption of the work. The fuel consumed is 8 parts small gas-coke for the gas-producer and 3 or 4 parts coal for raising steam for the exhauster, to produce 100 parts acid of 1·838 from such of 1·58. There is no weak acid and no cooling-water; the apparatus takes up very little space and requires hardly any repairs. The acid is quite limpid and free from nitrogen compounds.

In 1902 quite a number of Kessler furnaces were at work in England, and they were exceedingly well spoken of, both by the proprietors of the works and the Alkali Inspectors. Comp. *e. g.* Alkali Report No. 38, pp. 74 & 146.

The Kessler furnace gives no trouble of any kind; the escape of acid in the "vesicular" form is entirely prevented by the dry-coke scrubbers, and there is no loss by weak distilling acid, all of this being recovered in the "recuperator." Even acid of 100° Tw. can be brought in one operation to a strength of 95 per cent.

H_2S, and perfectly limpid. This apparatus has found extensive application during late years, both in England and on the Continent, and has replaced many other systems.

A patent of Dreyfus and the Clayton Aniline Co. (B. P. 788, of 1902) has a similar object as Kessler's "Recuperator," but deals with acid-vapours by themselves, unmixed with flue-gases and without the use of an exhauster or ejector. These vapours are conducted against the weaker acid run in for feeding the concentrating apparatus, for instance in an acid-proof column from 4 to 8 feet high, containing acid-proof material. The distilling vapours enter at the bottom, and no, or but very little, weak acid or noxious fumes issue at the top. They prefer the apparatus described in specification No. 11,544, 1898 (comp. p. 889), to be connected with this contrivance, but any other arrangement may be used.

In 1900 Kessler patented a modified apparatus (E. P. No. 21,376) for the same purpose. This apparatus, called a "Radiateur," is shown in figures 414 to 419. Its salient feature consists of fireproof slabs, heated from above and radiating that heat upon a thin stratum of acid placed a little below. *a* is a fireplace for coke or coal; *d, e, f, g, h,* the flues through which the fire-gases travel before reaching the chimney *i.* *o* is an arch from which the hot fire-gases radiate below upon the slabs *d*; through *f* they rise into flue *g,* covered by cast-iron plates *k,* upon which the lead pans *j j* effect the ordinary preliminary concentration.

The acid to be concentrated is kept in a flat trough *c* made of Volvic lava, or other material refractory to hot acids, with joints made tight by means of asbestos cement. This vat is surrounded by another vat, *r,* made of lead and resting on iron rails, *s.* The surface of the acid in *c* is kept at a distance of from 2 to 6 centimetres from the slabs *d d* by means of a valve in the entrance-pipe. The acid comes from the pans *j j* through siphon *g* and enters through pipes *y y* into an acid-proof chamber *m,* filled with silex fragments and jacketed with lead. The vapours not condensed here pass into a second chamber, *l,* made of lead and filled with dry coke (beginning with large pieces, gradually diminishing to the size of a grain of wheat), where the vapours are scrubbed and all the sulphuric acid is retained. This weak acid passes back through *p* into the pans *j j,* or elsewhere. From *l* rises a lead pipe, *u,* in which artificial draught is produced by injector *v* to such an extent as to balance the suction of chimney *i.* 2 is

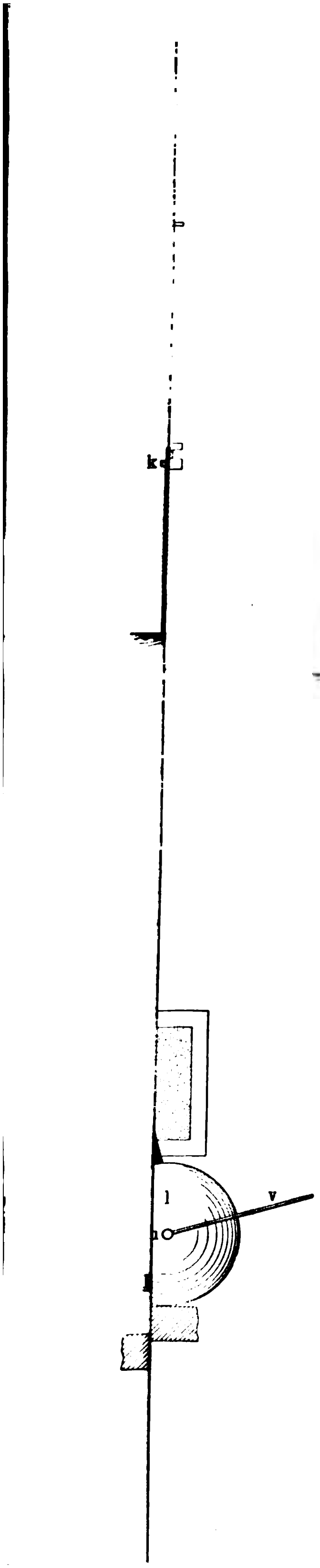


Fig. 416.

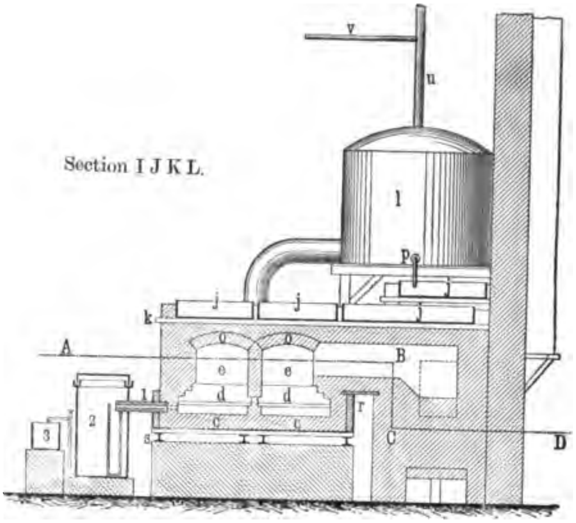
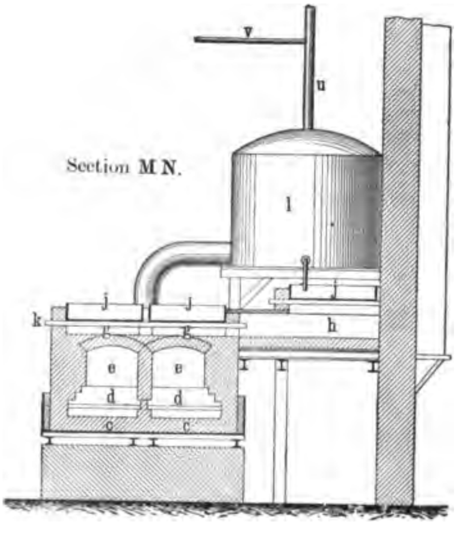


Fig. 419.



a lead cooler with hydraulic joint (similar to that employed in Kessler's hot-air apparatus); 1 a running-off pipe for the concentrated acid, made of Volvic lava covered with cooled lead, burnt on one side to the lead acid-basin and on the other side to the cooler 2. 3 is a lead pot for collecting the acid.

The process is worked as follows:—The acid is concentrated in pans *j j* to 60° or 62° B., and passes into the Glover-like scrubber *m*, where it meets the vapours formed underneath the slabs *d d*. It arrives hot in the trough *c*, where it is concentrated by radiant heat as it flows forward, so that it issues at full strength through 1 into cooler 2. The vapours are partly condensed in the silex scrubber *m*, by contact with the acid running through it, and then pass through the dry-coke scrubber *l*, from which the condensed acid runs away through *p*. The draught in *u* is regulated in such a manner that the air cannot take the opposite way, down *u* and through the interstices in the slabs into chimney *i*. It is also possible to allow some of the fire-gases to pass underneath the slabs *d d*, by means of interstices left on purpose, preferably near the entrance of the acid. Even all the gases may be conducted this way, but then the chambers *m* and *l* must be made much larger. In this case the heating must be done with coke; but if the slabs *d d* are closely jointed, or if the draughts are properly regulated, wood, coal, oils, or tar may be employed as fuel.

Zanner (B. P. 2379, 1902) employs cast-iron pans, lined with acid-proof slabs, the joints being cemented with asbestos cement, the corners &c. being strengthened by protecting pieces so that the primary joints are nowhere exposed to the acid. These pans are placed in the flues leading the gases away from the pyrites-kilns and are fed with Glover-tower acid, which is thus brought up to 93 p. c. H_2SO_4 without any extraneous fuel, according to the assertion of the inventor. To protect the acid from flue-dust, the pans are covered with perforated iron (?) or fire-clay slabs. The acid is compelled to flow in a zigzag direction by means of suitable partitions.

According to information received from the inventor in February 1902, a set of two pans, 1900 × 400 mm., is capable of supplying per diem 4 tons of acid of 66° B. from a mixture of $\frac{4}{5}$ Glover-tower acid, $\frac{1}{5}$ chamber-acid. The pans had been working continuously for five months, except two cleaning shifts purposely interposed. The weak-acid pan lasted five months, the strong-acid pan seven months, and both might have lasted longer if mistakes had not been made in the lining which can be easily avoided in future.

Fig. 420.

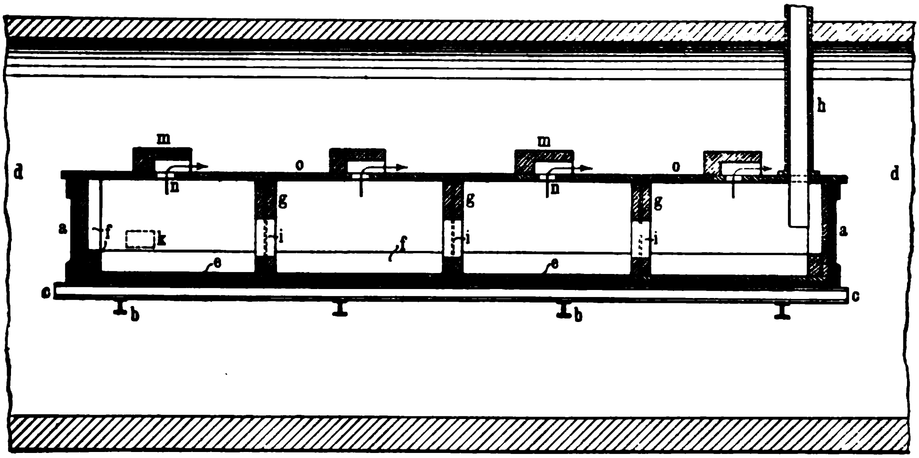
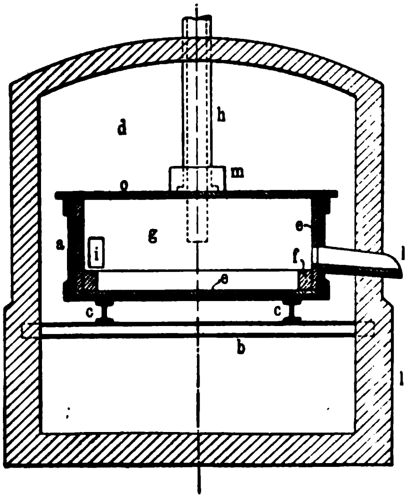
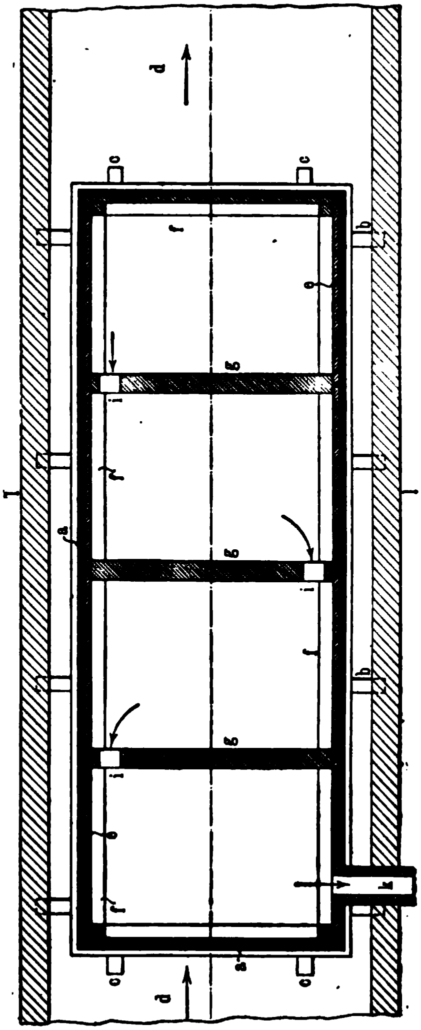


Fig. 421.



The acid obtained was clear and but slightly yellow. The temperature in the gas-flue containing the pans was about 400° C. The cost of renewing the pans (of course there is nothing to pay for

Fig. 422.



fuel) up to the present amounts to 1*s.* 6*d.* per ton of concentrated acid, apart from patent royalty.

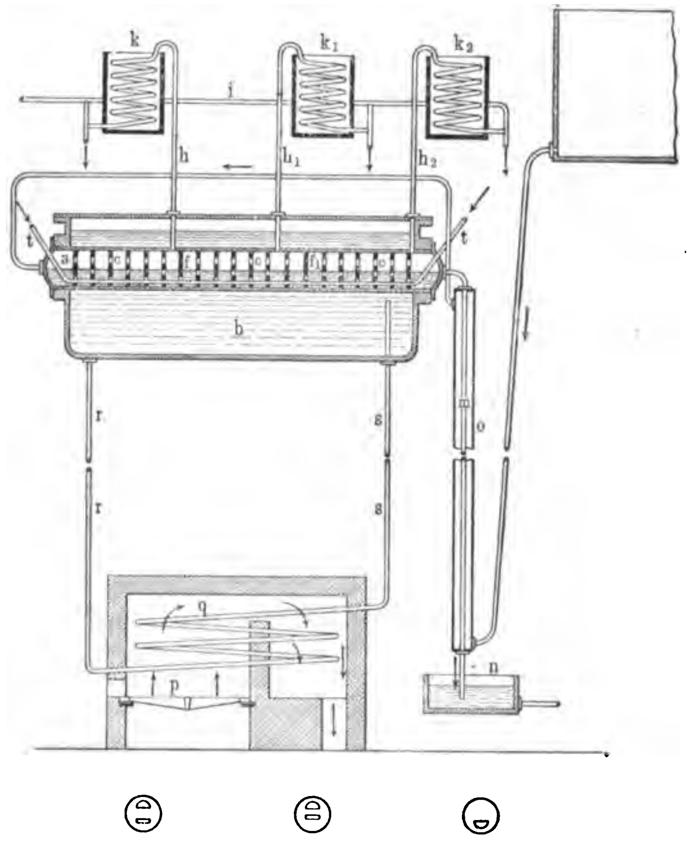
Figs. 420 to 422 show this apparatus. In the flue *d,* on iron bearers *c* and *b,* rest the cast-iron pans *a,* lined with stoneware plates *e,* cemented with asbestos and silicate of soda. The size of the plates is chosen in such a manner that the joints are covered by the upright stone plates *g,* which hold down the bottom plates in their places, and which also cause the acid to run in a zigzag stream, by the openings *i i* (comp. the sectional plan fig. 422). The corners are secured by stones *f f,* so that no primary joints are exposed to the acid. The pans are covered by plates *o,* with holes *n,* protected against flue-dust by caps *m.* Where acid of 97 or 98 p.c. is to be made, several pans are combined, the first of which has no stoneware lining on its bottom. The acid is fed in by the porcelain-lined iron tube *h,* and it leaves by the cast-on lip *k* lined with stoneware passing through the brickwork *l.* The steam and acid-vapours pass along with the pyrites-kiln gases into the Glover tower; also any nitrous vapours, when waste nitrating acids (from nitrobenzene, nitroglycerine, &c.) are to be concentrated. It is best to provide a by-pass for the kiln-gas, for the purpose of cleaning or repairing the pans. The yield of acid of 55½° B. per square metre (10·76 square feet) of pan-bottom per 24 hours is from 30 to 48 cwt., according to the heat of the gases and the feeding-acid, and its previous concentration. Much more work could be performed when working the apparatus with a vacuum; and it can be also worked by any other source of heat. There is absolutely no expense for fuel, and next to none for supervision; the cost of plant is very slight.

W. R. Quinan (U.S. P. 699,011; Journ. Soc. Chem. Ind. 1902, p. 772) constructs behind the pyrites-kilns a "mixing-chamber," provided with an iron roof, covered with infusorial earth or the like, which near its top leads to an ascending inclined flue, the bottom of which is formed of steps made of Volvic lava. These steps possess upwardly extending flanges at the back and sides, and a downwardly extending lip or flange at the front end, overlapping the back flange of the next lower step. This inclined flue may be connected directly with the first chamber or, preferably, with the Glower tower, from which the acid runs down the Volvic steps, and arrives in a highly concentrated state in the mixing-chamber.

Concentration of Sulphuric Acid in Vacuum-Retorts.

A very interesting concentrating method, including the use of Field tubes, formed part of an ingenious, but over-complicated system of the manufacture of sulphuric acid invented by De Hemptinne, of Brussels, and described at length, with diagrams, in our first edition, pp. 507 to 512, to which description we simply refer, as De Hemptinne's process has never been carried out in

Fig. 423.



full and is decidedly impracticable. Another ingenious process of his, described and illustrated in our first edition, pp. 513 to 516 seeks to carry out an idea previously proposed by several other inventors, *e. g.* Kuhlmann (in 1844), viz. concentrating sulphuric acid in a *partial vacuum,* and thus reducing the temperature to such a point that the whole operation can be carried on in lead. As this process, which was actually at work for some time, has not proved successful, we also refer for it to our first edition. A further modification of his plan has been described by De Hemptinne in the 'Bulletin du Musée de l'Industrie de Belgique,' January 1882.

Of more modern forms of leaden vacuum-apparatus we shall mention that of Krell (G. P. 118,880). The acid flows through a lead pipe *a,* fig. 423 (p. 913), heated by an oil-bath *b.* Pipe *a* is stiffened inside against atmospheric pressure by diaphragms *c c,* leaving passages for the acid in such a manner that the acid must proceed in a zigzag course, and provided with communications in their upper part for the vapours. At the bottom of pipe *a* lies a perforated pipe *t,* through which hot gases may be introduced for the purpose of hastening the concentration.

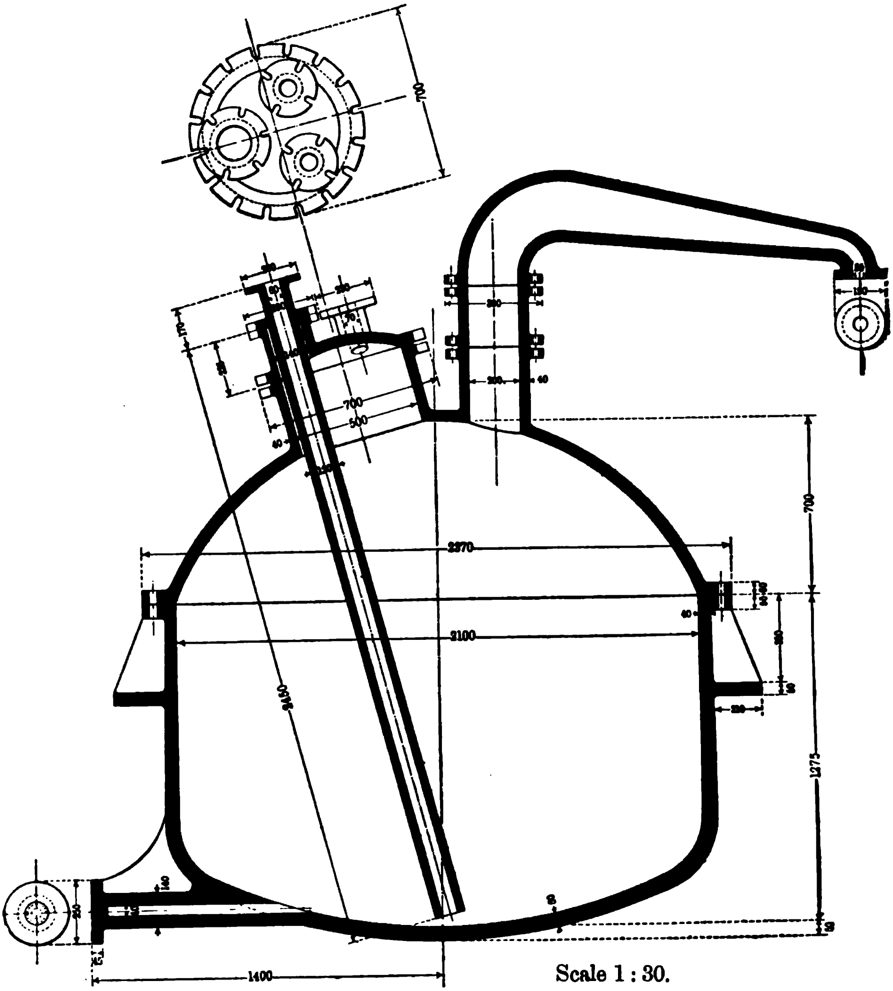
The unperforated diaphragms $f\,f_1$ stiffen the pipe and divide the steam-space into three compartments, connected through $h\ h_1\ h_2$ with a common vacuum-pipe *i.* In this way the coolers $k\ k_1\ k_2$ will condense acids of various strengths. The acid entering as chamber-acid of 50° B., leaves as acid of 64° or 65° B. [that is, we must notice, only 86 to 90 p. c. H_2SO_4 !] and descends through a pipe *m,* which must be at least 17 feet long, into a collector *n.* By surrounding *m* with a jacket *o,* the heat of the outflowing acid can be utilized for heating up the chamber-acid. Oil-bath *b* is heated indirectly by means of coil *q,* heated by a fire *p,* and connected at both ends, *r, s,* with the oil-bath in such a manner that a constant circulation takes place. [According to private information, Krell employs lead alloyed with a little copper, as recommended by me for higher temperatures and strengths, comp. p. 209.]

Cast-iron retorts are also used to concentrate sulphuric acid in a vacuum, starting from such strengths at which the cast-iron is not yet acted upon.

Fig. 424 shows the shape of cast-iron vacuum-retorts used in Germany for sulphuric acid with great success and furnishing very high-strength acid. Such a retort weighs about 7½ tons.

I. Meyer (G. P. 71,580) combines a lead vessel with an iron vessel; the latter, which receives the acid in an already concentrated state, communicates with the air-pump. The pan-bottom is slightly inclined to one side. The dilute acid comes in contact only with lead, the strong acid with iron or platinum. The concentrating-apparatus is best connected with a distilling-apparatus

Fig. 424.



Scale 1 : 30.

working at the same vacuum, and continually receiving the concentrated acid through a siphon.

Brown and Georgeot (French pat. 241,815) state a theory as to the concentration *in vacuo* in which there is nothing new.

The Kommanditgesellschaft L. Kaufmann & Co. (G. P. 134,773) concentrate sulphuric acid in a cast-iron vacuum-still by means of a steam-jacket or gaseous fuel, driving it over the heating-surface in layers of only 10 to 15 millimetres depth by means of stirrers almost touching the metal, with such a velocity that the concentrated acid by its centrifugal force can issue continuously in spite of the vacuum. By the above treatment the steam-bubbles are more easily detached from the solid surfaces.

Cast-iron vacuum-retorts are most suitable for treating the *dirty acid* (acid-tar, sludge-acid) formed in the chemical treatment of mineral oils (comp. p. 897). This acid, when boiled for some time, chars most of the organic substances dissolved by it, and is at the same time concentrated. But in this process much of it, sometimes nearly 20 per cent., is reduced to SO_2 (comp. p. 898), which causes not merely loss, but also great nuisance, unless the SO_2 can be re-converted into SO_3 (comp. Chapt. XI.) or otherwise utilized. This difficulty is overcome by the employment of vacuum-retorts. The considerable lowering of the boiling-point thus produced causes the action of the acid on the organic substance to be much less and of a different kind. There is only about 3 per cent. lost as SO_2, and the organic substance is converted mostly into a carbonaceous substance which can be removed by filtration through sand. The acid thus made is = 66° B.; it is dark-coloured, but quite fit to be used over again for the refining of mineral oils.

Kynoch & Co. and Cocking (E. P. 28,891, 1896) employ cast-iron retorts working with a vacuum for the concentration of waste acid from nitroglycerine.

Concentration of Sulphuric Acid by Electricity.

Bucherer (Chem. Zeit. 1893, p. 1597) makes the following calculation:—The production of 100 kil. acid of 66° B. from 117 kil. acid of 60° B. requires 32,679 large calories, corresponding to

$$\frac{32679 \times 4{\cdot}2 \times 10^3}{736 \times 3600} = 44{\cdot}2 \text{ electrical H.P. hours;}$$

calculating the electrical H.P. hour=½*d.*, the above is equal to £1 per ton (on the large scale). Further estimates of the amperage and voltage, the platinum surface, &c. must be passed over here as being entirely hypothetical.

Häussermann and Niethammer (Chem. Zeit. 1893, p. 1907) have made actual experiments on this point. As might be expected, only alternating currents can be employed, since otherwise an electrolysis takes place. The concentration is very easy, but requires 1490 watt-hours per kil. This seems to exclude every possibility of practical application.

Peuchen and Clarke (Engl. pat. 24,739, 1893) propose both purifying and concentrating sulphuric (and acetic) acid by the electric current, eventually proceeding up to distillation. They proposed electrodes mechanically revolving round a hollow shaft within the boiling acid! A fresh patent of theirs (Germ. pat. 83,526) describes stationary electrodes for the same purpose.

Wacker (Engl. pat. 3183, 1895) proposes concentrating sulphuric acid by electricity, with introduction of SO_2.

General Remarks.

Loew (Zsch. angew. Ch. 1896, p. 259) gives some calculations with respect to the work done by concentrating-apparatus for sulphuric acid. In the case of platinum stills the work performed is in inverse proportion to the strength of the acid distilling off; the stronger the distillate, the less concentrated acid is produced, although even more fuel is consumed in the former case. Any contrivances, like Prentice's corrugated bottoms or partitions, inside a long still which diminish the mixture of the dilute acid entering and the concentrated acid leaving the still are useful in this direction. Turning to the concentration by hot air or fire-gases, we can calculate the amount of fuel required, if we ascertain the necessary data. Thus, for instance, if the gas leaves the apparatus at a temperature of 80°, and saturated with steam, we shall require 6·12 parts of carbon to produce 100 parts acid of 95·6 per cent. from the corresponding quantity of acid of 64·5 per cent., assuming the latter to enter at 20° C. and the former to issue at its boiling-point. Fuel producing steam during its combustion is less advantageous than coke.

Monohydrated Sulphuric Acid.

For some purposes sulphuric acid containing no water, or hardly any, and corresponding as nearly as possible to the formula H_2SO_4, is required. Such acid is extremely useful in certain nitrating and sulphonating operations, connected both with the manufacture of explosives and that of colouring-matters. So great, indeed, has been the want of such a monohydrated acid, that many manufacturers made it from ordinary rectified oil of vitriol and Nordhausen fuming acid, in which case the SO_3 contained in the Nordhausen acid combines with the excess of water existing in the rectified O.V. to form H_2SO_4. This was, however, formerly a costly process, as is shown in our 2nd edition pp. 738 and 739, and therefore I worked out another process. At the present day the cheapening of fuming O.V. produced by the contact method makes this process unnecessary, but as it is carried out on a new principle we shall retain its description here.

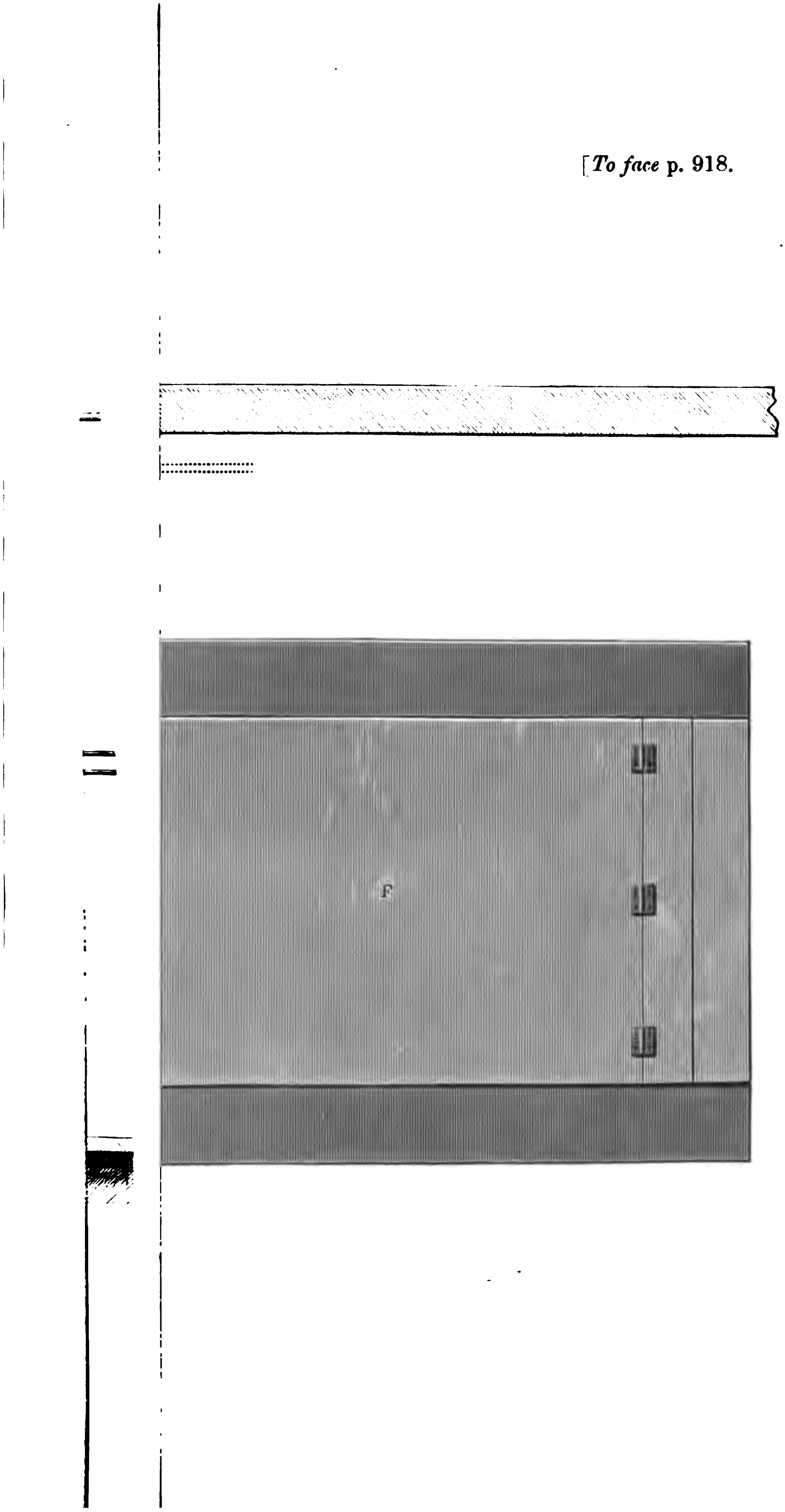
My proposal, *freezing* out the monohydrate from good rectified O.V. (E. P. 96, 1883, and 4430, 1887, the former communicated to Walter Weldon, the latter to John Brock), has been carried out with full success at several alkali-works.

Sulphuric acid is concentrated in platinum or iron stills to 97 per cent. H_2SO_4, or a little more, if convenient, and is then cooled down in the usual manner. It is then conveyed by air-pressure or in any other suitable manner to the store-tank A, placed at a somewhat higher level than the "charging-box" B of the freezing-machine (figs. 425–428). Instead of running the acid directly from A into B, it is conveyed down to the ground-level in a conduit C, in which is interposed a cooling-worm or other refrigerating contrivance D. The pipe C, with an interposed shutting-off tap E, rises a little above the top of the charging-box B, and then descends into the top of this box. The object of tap E is to shut off the communication between A and B during the time a charge is being blown out of B.

The charging-box B is made of iron and of such a shape that it stretches from side to side right across the tank containing the freezing-cells. It is divided by vertical partitions into the same number of divisions as that of one row of iron freezing-cells G, and each of these divisions is made of such size that on blowing out its contents it exactly fills one of the cells G to a suitable height. The partitions do not reach quite up to the lid of the charging-box B, so that all the divisions are filled by the supply-pipe C from the store-tank A, and their contents are forced out

Lu

[*To face* p. 918.



simultaneously by means of the compressed air acting through a pipe K inserted into the lid of the charging-box. Pipe K rises to a higher level than the top of the store-tank A before descending to the air-pump; consequently when A is put into communication with B, the acid fills the entire box B and rises in the air-pipe K up to the level of the store-tank, but it cannot overflow into the air-pump. Pipe K is provided with two taps, of which L communicates with the air-pump, and M with the open air; the latter tap is opened while the box is being charged with acid, and is shut immediately afterwards.

Each of the divisions of box B is provided with a discharge-pipe H, which begins immediately over the curved bottom of the box, passes out of the lid, and rises upwards so far that no acid can overflow during the charging of B from the store-tank A. The discharge-pipes H H then descend side by side, so that the lower end of each is just above one of the freezing-cells G. Thus, as soon as the compressed air begins to act upon the surface of the acid contained in the box, all the discharge-pipes begin to play simultaneously, and all the freezing-cells belonging to that particular row are filled at the same time. When this has been done, a leaden dish J is brought underneath the ends of the pipes, to catch the acid draining out of them and convey it away. The row of freezing-cells, which is suspended in an iron frame N, is moved by means of a travelling-crane O to the other end of the freezing-tank F, which contains a number, say 10 or 15, of such rows of freezing-cells. The space between the cells is filled with a solution of calcium chloride, kept at a low temperature, say – 20° C., or somewhat more or less, by means of any convenient cold-producing machine. Each time a fresh row of cells has been filled the frames containing the other rows, which rest on pulleys, are moved towards the front end of the tank, so as to allow of the last row of cells being lowered into the back part of the freezing-tank.

When the row of cells which has been longest in the freezing-tank has been sufficiently cooled down, it is lifted out by means of the travelling-crane O. The cells are then dipped for a few seconds in a vessel containing warm water, in order to detach the frozen mass from the sides of the cell by superficial fusion; and when this has been effected the cells are lifted out and are tilted into a spout or trough P, care being taken to prevent any of the water adhering to the outside of the cell getting into the spout.

The spout P contains an Archimedian screw Q, which crushes up the frozen mass and conveys it into a cast-iron centrifugal machine R, placed beside the apparatus. The cells G are then righted again and are ready to receive another charge of rectified oil of vitriol. By the action of the centrifugal machine R the frozen mass is rapidly separated into a white crystallized mass of monohydrated sulphuric acid and a mother-liquor consisting of less concentrated acid. The latter is either sold in this state (it is equal in strength to good rectified O.V.), or is brought up to full strength by the ordinary processes of concentration. The solid monohydrate is scooped out of R into a pan S, made of iron enamelled inside, and surrounded by a warm-water jacket; here it is melted and is, by means of a tap, run out into carboys or other vessels intended for storing and carrying the product.

The just described process for manufacturing monohydrated sulphuric acid by freezing was carried out on a large scale in Germany (Griesheim), France (Petit-Quevilly), and England (Widnes) and worked for many years. Only in 1900 it was given up at Griesheim, having become unremunerative through the cheapening of fuming sulphuric acid in consequence of the development of the contact processes for the manufacture of sulphuric anhydride.

Osterberger and Capelle describe this process, as carried out at Petit-Quevilly, almost exactly as above (Bull. Soc. ind. Rouen, 1889, p. 307; Journ. Soc. Chem. Ind. 1890, pp. 390 & 507).

A proposal by Messel (E. P. 1201, 1878) to prepare monohydrated sulphuric acid by passing pyrites-kiln gases through concentrated sulphuric acid, in order to absorb the SO_3 contained in the gases, need only be mentioned here.

Packages for Sulphuric Acid.

Sulphuric acid was formerly always, and is even now to a great extent, sent out in large glass bottles or *carboys* of about 15 gallons capacity, packed in baskets with straw, the projecting necks being still further protected by straw ropes. They are closed by earthenware stoppers dipped in melted brimstone and put in quickly before the sulphur has solidified. Mostly damp clay is put round the top and a linen rag is tied all over it. Often, lly for short distances, the brimstone is omitted. The only last a short time when exposed to the weather and the damp soil, and especially when any acid gets at them. This last is sometimes difficult to avoid: after once using, a few drops of acid run down the neck of the carboy and find their way to the bottom of the basket; and the floor of the warehouse, where they are placed, is not easily kept entirely free from acid. Therefore the bottom of the basket is damaged first; and on lifting the carboy the bottle filled with acid forces out the bottom of the basket by its weight and falls through. For this reason a damaged basket ought never to be sent out; some works go upon the principle of *always* packing the returned carboys in fresh baskets. The baskets stand much longer when they are dipped two-thirds of their height in coal-tar. In England, baskets made of stout iron wire or of thin hoop-iron are now common, protected against quick rusting by a thick coating of coal-tar. In the north of England frequently, sometimes also in Germany, carboy-tubs are used, made of small staves, tapering a little downwards, and bound with iron hoops; the bottle is put in, packed in straw, with only its neck projecting; a circular cover, provided with a hole for the bottle-neck, is put on and fixed. These tub-carboys are rather clumsy and somewhat dearer than basket-carboys, but are much more durable; and they afford the great advantage that railways, barges, &c. carry them in two tiers one above the other, which they never do with basket-carboys.

In America, cubical cases are employed, kept together by iron hoops; the bottles are put in with sea-weed; they cost one-third of a dollar per cwt. In France, and also at Aussig in Bohemia, stoneware jars of the size of ordinary glass carboys, and of the same clay as is used for "bombonnes" (acid-receivers), are frequently employed; these can be moved about at the works without baskets, but must be put into baskets for sending out. At Beauvais, where they are made, they cost 1½ franc each.

Sometimes the glass carboys are surrounded with infusorial earth, which in case of breakage absorbs the acid, whilst with straw-packing it runs out and may injure the men or damage railway-trucks. (This way of packing is especially useful in the case of nitric acid, which may cause a fire when coming into contact with straw.)

A special kind of carboy-hampers has been patented by Garneri (E. P. 3190, 1883). "This basket is built up of numerous standards of wood, thin and elastic. The base is preferably composed of two conical and concentric rings, thin, and of 5 to 6 centimetres (=2 to 2⅜ inches) in diameter. The standards are bound and fixed at equal distances between the two conical rings. Wooden rings, placed at intervals in the height of the basket, are fixed both on the exterior and interior by means of a jointed mould, which gives to the basket the desired contour, according to the carboy or other article it is intended to contain."

Schleicher (G. P. 18,112) employs tight-fitting wickerwork baskets, the upper part of which is removable and is connected with the lower part by wire fastenings. This plan is shown in fig. 429. *b* indicates the glass, *e* the joint between the two parts of the wickerwork, e_1 the removable part of the latter, *c d* the cover.

Fig. 429.

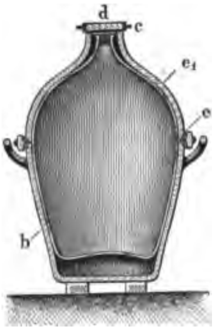
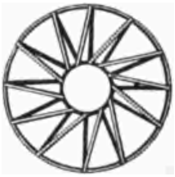


Fig. 430.



The Marple Chemical Company, Marple near Stockport, sells "Carboy Protectors" for the tops of acid-carboys, as shown in fig. 430, which admit of stacking up to four tiers of carboys over one another without any risk of breakage.

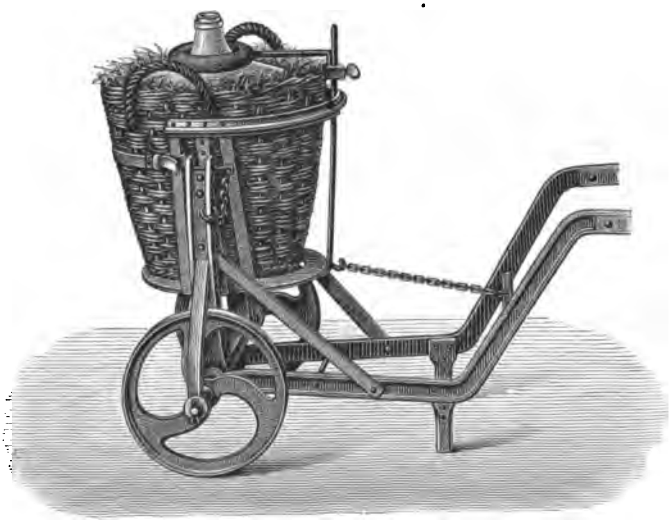
Mauser (E. P. 11,095 and 21,986, 1902) provides the hampers with a top kept down by springs, or suspends the carboy in the hamper by springs.

Junckers (Chem. Zeit. 1902, p. 582) employs for *filling* acid-carboys a new kind of funnel, closed at the top. Only two openings are left, one of them for inserting the pipe or tap from the filling-vessel, the other one, provided with a neck, for conducting away any vapours formed. By making the joints with the feeding-pipe or tap and with the neck of the carboy tight by means of india-rubber washers, any loss and damage to the carboys through acid splashing about is avoided.

Several contrivances have been invented for *emptying acid-carboys*. Some of them consist of iron frames adapted for tilting, others of apparatus adapted to the carboy-necks and acting on the principle of a chemist's wash-bottle, the necessary air-pressure being produced by a small force-pump or by an india-rubber bag with treadle. These and other contrivances are described by Oppler in his report on the Berlin Exhibition of Apparatus for preventing Accidents (Chem. Ind. 1889, p. 528). Comp. also the siphons &c. shown p. 502 *et seq.*

The Aktiengesellschaft für Anilinfabrikation at Berlin has patented (G. P. 8305; Wagner's Jahresb. 1880, p. 236) an apparatus for carrying acid-carboys without in any way putting stress on the handles or other parts of the hampers, so that the carboys can be safely handled even in rotten hampers. Other contrivances of this kind consist of hand-trucks, on which the carboys are suspended from chains, as shown in fig. 431.

Fig. 431.



Nevertheless it frequently happens that glass carboys get cracked, either in handling or by the jolting of railway-trucks; and the acid running out is not merely lost, but often does a great deal of damage. The railway and steamboat companies accordingly will only accept acids (sulphuric acid, as well as other mineral acids sent in carboys) at the sender's risk, or else at very high rates for carriage, and only send them by certain trains. Under all circumstances, on account of the bulky nature of this merchandise, a very much higher rate is charged for its conveyance than corresponds to its weight. A truck which carries 10 tons of goods in casks can only carry about 2½ tons of vitriol in carboys. The additional cost of carriage is therefore in direct proportion to the accompanying dead weight and bulk; and as such the water must be regarded which is contained in acid of 144° Tw. (brown vitriol) over and above that in strong vitriol.

The cost of carboys also amounts to a good deal. It differs very much, according as the situation is more or less convenient for purchasing the bottles &c.; but it will hardly ever be under £2 per ton of real acid, and is much higher for brown vitriol containing 78 per cent. of SO_4H_2 than for strong vitriol with 93 per cent. of SO_4H_2. Of course, the empties are mostly returned; but there is always much breakage, and for longer distances the return-carriage is too dear.

It follows from this that it will only pay for a certain distance, differing very much according to local circumstances, to send out brown vitriol of 144°–152° Tw. in glass carboys; when the distance exceeds that limit, the extra cost of packages and transit becomes equal to or more than the cost of extra concentration, and the consumers prefer to buy strong vitriol of 168° Tw. Habit or, more strictly speaking, ignorance causes some consumers to buy acid of 168°, when 140° or even chamber-acid would do quite well.

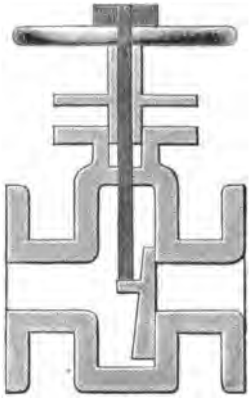
For large consumers, and especially for sending great distances by land, glass carboys are not now employed for the carriage of sulphuric acid. For some time leaden or copper vessels were used for this purpose, but these have been abandoned for *wrought-iron vessels*, more especially *tank-waggons*. Balmain and Menzies patented in 1869 this way of carrying sulphuric acid, which, however, seems to have been previously in use locally; its general use appears to date from about 1880. The stronger the acid the less danger is there of any action upon the iron; but even down to 130° Tw. it can be safely carried in iron, provided there are no injurious impurities present, such as nitrous acid, and that the air has no access—the latter, because its moisture condenses on the surface of the acid, forms a layer of dilute acid, and corrodes the iron in that place.

The iron acid-tanks are sometimes made of an angular section, like ordinary railway-trucks; but these have been almost entirely superseded by cylindrical boiler-shaped tanks of 10 tons capacity. A great advantage of the latter is, that they resist pressure, and that, at the consumer's works, they can be fitted with an arrangement for forcing the acid out of them into a store-tank on the premises, so that the tank-waggons are at once emptied and can be sent back to the seller's works. Smaller tanks of this kind, say holding 2 or 2½ tons, can be used for road-traffic.

Nörrenberg (Chem. Ind. 1896, p. 553) gives special instructions for cleaning out tank-waggons used for sulphuric acid.

Iron tank-waggons can be used for concentrated acid as well as for chamber-acid. The thickness of the plate for acid down to 140° Tw. is generally $\frac{3}{8}$ to $\frac{7}{16}$ inch, for chamber-acid $\frac{5}{16}$ inch. The plates must be very well rivetted together and tightly calked, as any leakage of acid will cause a strong corrosion on the outside, in spite of the self-evident precaution of keeping the iron very well painted with coal-tar varnish. For the same reason the tanks, when empty, must be kept tightly closed; any portion temporarily exposed to the air, *e. g.* manholes &c., should be covered with sheet-lead.

Fig. 432.

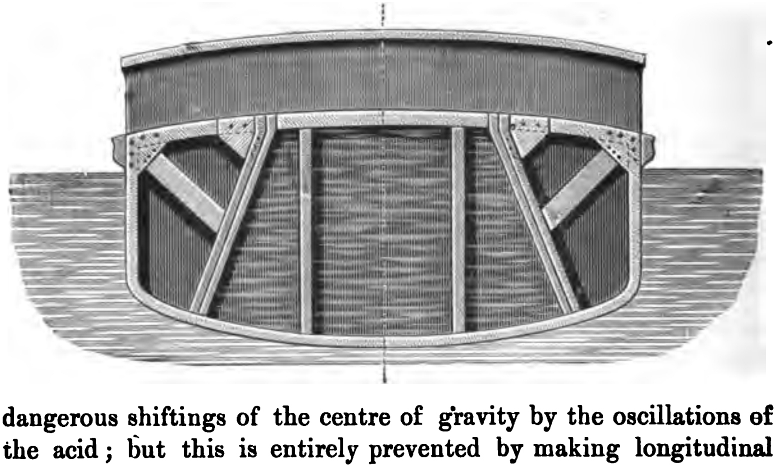


The emptying takes place by means of a siphon, or else by an angular valve-tap as shown in fig. 432, or by an india-rubber hose closed by a strong clamp. India-rubber, however, should be employed only for chamber-acid. The valve is made of gun-metal (ordinary, not phosphorus bronze which does not resist the acid so well); the iron spindle is cased with hard lead up to the screw-thread, the stuffing-box is packed with asbestos.

In spite of all precautions, a little gas is generally evolved in acid tank-waggons made of iron, which, in opening them, may cause some acid to splash about and injure the men. This is avoided by a contrivance constructed by Vorster and Grüneberg (Oppler, Chem. Ind. 1889, p. 528). On the top of the boiler-tank there is a pipe, and within this another pipe, closed at bottom and open at the top. The annular space thus formed is closed at top and open at bottom. The inner pipe has two lateral openings near its bottom; through these the gas collected in the boiler-tank gets into the inner pipe and thence escapes outside, whilst the acid carried along collects in the annular space between the pipes and runs back again.

Where the acid has to be carried on canals, the boats may be arranged as tanks by lining them with lead (which in such cases is much more suitable than for railway carriage) or even with iron. As was shown by Kuhlmann, jun., in 1878 (Chem. Ind. 1879, p. 333) such boats when used for this purpose are subject to dangerous shiftings of the centre of gravity by the oscillations of the acid; but this is entirely prevented by making longitudinal partitions, leaving an air-space widening out at the top, as shown in fig. 433.

Fig. 433.



Holden (Engl. pat. 3805, 1877) proposes to construct acid-tanks from wood which has previously been warmed and soaked with paraffin. The edges are to be made tight by a solution of gutta-percha in naphtha.

For *sea-transport* wooden boxes lined with lead are usually employed; iron would probably answer better.

Vorster and Grüneberg (G. P. 24,748) have proposed the following plan, especially with a view to sea-carriage :—Dry and finely divided *kieselguhr* (infusorial earth) is saturated with three or four times its weight of strong sulphuric acid. The product, which thus contains at least 75 per cent. of acid, retains its pulverulent form and can be transported by land or sea in lead-coated sheet-iron vessels without any risk of breakage. When it reaches its destination the mass is either used directly or is diluted with water, and the acid is separated from the kieselguhr. This plan has not been found very practical, nor does it seem to be called for, as the pure (liquid) acid itself can be sent out perfectly well in sheet-iron vessels closed by screw-plugs.

White and Rickman (E. P. 17,095, 1887) for a similar purpose mix sulphuric acid with anhydrous sodium or magnesium sulphate (hydrochloric acid with calcium or magnesium chloride), dissolving the salt in the acid by the action of heat, and allowing it to solidify on cooling. The salt frequently does not interfere with the use of the acid. This plan is evidently not practical.

CHAPTER X.

ARRANGEMENT OF A SULPHURIC-ACID WORKS ON THE CHAMBER PLAN; YIELDS AND COSTS.

Although it is obvious that no fixed rules can be laid down as to the way in which a sulphuric-acid works should be planned, yet a few remarks upon this subject may be of some use. In the first place, the arrangement of acid-works depends upon whether they are to supply only chamber-acid or acid up to, at most, 150° Tw., or rectified O.V. The first case, which is that of manure-works, and even of some salt-decomposing works, is, of course, the simplest, no concentrating-apparatus whatever being required. Formerly such works usually did not possess any, or only small, Gay-Lussac or Glover towers. But although the latter in this case are not called upon to furnish a larger quantity of strong acid than is needed for the Gay-Lussac tower, and as they do furnish much more than that, water has sometimes to be used in order to bring the acid down to the strength required; yet it is most irrational, in view of the waste of water, the yield of acid, and even the nuisance produced by noxious vapours, to work without any or without fully efficient Glover and Gay-Lussac towers.

Where acid concentrated up to 140° or 150° Tw., but of no special degree of purity, is required (that is, generally in works decomposing salt and for a few other purposes), it is easy to obtain the whole of the acid of that strength without any special concentrating-apparatus, by means of Glover towers. Where, however, purer acid has to be made, either for sale or for further concentration in glass or platinum, concentrating-pans must be provided. These may be heated either by the heat of the brimstone- or pyrites-burners, and are then of course placed over these, or else over the flue conveying the kiln-gases to the Glover tower; in either case no separate ground-space is required for them.

Or else (which we deem unnecessary in all ordinary cases) they are heated by special fires, either from the top or from the bottom, or by steam. Most frequently room will be found for this under the acid-chambers or immediately adjoining.

Finally, where rectified oil of vitriol is made, this can be (and in many cases is) done underneath the chambers; but more usually, especially in the case of glass retorts, a special retort-house is constructed for this purpose.

Without taking any further notice of the last concentration of the sulphuric acid, we remark as follows on the arrangement of the remaining apparatus. The lowest level is always occupied by the pyrites- (or brimstone-) burners; only there must be space left for wheeling away the cinders. Accordingly the burners are always erected on the ground-level; and the stone-breakers, if present, are mostly found on the same level. The pyrites in large works arrives on a railway resting on trestles (gears) and is tipped between the trestles, in order to be taken away as it is wanted, to be broken and laid in front of the kilns. Where the supply of ore is quite regular, the stone-breaker can be disposed so that the ore will pass direct from the railway-trucks through the breaker, and arrive broken on the ground-level, thus saving labour. Where the ore is broken by hand, or where it arrives in large and irregular parcels, this cannot be done very well.

Unbroken pyrites, especially non-cupreous, can be stored in the open air without much damage; but after breaking it should be protected from the rain. It is sifted directly after; the dust is stored apart from the lumps; and both are taken to the burners across a weighing-machine. The breaking, sifting, and storing of the broken pyrites nearly always takes place underneath the chambers. Where these are high enough above the ground, the burners themselves can be placed beneath them; otherwise they are erected in a separate shed immediately adjoining, and I would take this course even in the former case. Any cooling-pipes or tunnels are arranged along the side or on the top of the chambers. Where the burners are built under the chambers, the outer pillars of these must be connected by a light open-work wall, to keep the wind off the burners.

The nitre-ovens, where such are to be made, are always built at the end of each set of burners and as a continuation of it.

The steam-boilers are also sometimes placed under the chambers; but it is decidedly better to put them in a shed outside, both in order not to injure the timber of the chamber-bottom by steam leaking or blowing out of the safety-valves, and to save the boiler-plate from being corroded by any accidental droppings of acid. In case of an explosion the damage will then not be quite so serious as if the boilers stood directly under the chambers.

As the burners are built on the ground-level, as the chambers are in any case erected at a certain height above it, and as the gas-pipe also enters into the upper part of the chamber, the gas-pipe must necessarily rise a good deal; and the conditions of draught are thus satisfied.

If, however, a Glover tower is to be used, it must be placed between the burners and the chambers. Formerly a few burners were sometimes set aside for working the nitre-ovens by their heat and taking the nitre-gas direct into the first chambers; this is now rarely or never done, but each set of burners is followed by the nitre-ovens and then by the Glover tower. Where liquid nitric acid is employed, the nitre-oven is simply left out. The Glover tower itself must be placed with its base rather higher than the top of the gas-flue over the burners. In this way the burner-gas can travel horizontally to the tower; but it is generally made to rise a little higher and to descend slightly into the tower, so that any acid splashing into the pipe runs back into the tower. Usually the levels of the Glover tower and the chamber are planned in such a way that the gas issuing from the tower can still enter the chamber below its top. This secures good draught into the chambers, provided there is a sufficiently strong pull at the exit end. Where this is not the case, the indispensable draught in the pyrites-burners is sometimes brought about by taking the gas up a high Glover tower, or else upwards from the tower through a special pipe, and then down again through the chamber-top (comp. p. 682). In some cases injectors or fan-blasts are made to produce the necessary draught (p. 559).

On the other hand, the chambers are sometimes placed so high that the top of the Glover tower is below their bottom, and the chamber-acid can be run directly into the tower.

The chambers, as already mentioned, are either arranged so that their floors are all at the same level, or so that each following chamber is from 1 to 3 inches higher than the preceding one. A greater difference is not necessary, but is sometimes employed for local reasons. From the last chamber issues a pipe connecting it with the Gay-Lussac tower, which can only exceptionally be placed

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on a foundation so elevated that this pipe need not descend—certainly a preferable arrangement if the levels permit it. Provision must also be made for interposing a long cooling-channel between the last chamber and the Gay-Lussac tower, unless there is a special small chamber provided for cooling and drying the gas, which chamber receives no steam.

In any case the Gay-Lussac and Glover towers should be combined into a set, with the necessary tanks, air-pump, acid-eggs, &c. arranged at the foot, by which the attendance will be much facilitated. In large works with several sets of chambers it is preferred rather to combine several Glover towers, and in any case several Gay-Lussac towers, to form a set.

In the previous editions of this book drawings of a set of chambers with appurtenances were given to serve as a general guide for the observation of the just-mentioned rules. Not to speak of the first edition, even the drawings contained in the second edition are somewhat out of date now. Fortunately I am enabled, by the kindness of Mr. Niedenführ, to enrich this present edition with modern plans for two separate cases, drawn expressly for this book. The first case (figs. 434 to 437) is that of works on the old and hitherto most general style, where no special means are employed for diminishing the chamber-space. The plans show how such chambers and their belongings can be most suitably built in a climate where they must be enclosed in buildings. In England this is usually not done, but the alterations to be introduced in the latter case are easily understood (comp. pp. 441 & 448).

On the necessarily adopted small scale most details of construction and auxiliary apparatus cannot be shown, and for these we must refer to the 5th Chapter, where also the details of the French (p. 543) and American systems (p. 448) will be found.

The plant shown here is intended for the production of 20 tons real monohydrated H_2SO_4 per 24 hours, in the shape of the corresponding amount of chamber-acid. This is a somewhat large set, but Mr. Niedenführ considers it best to work on such a scale, if all modern improvements are applied. Since all dimensions are given (in metrical measure), the reduction to a smaller size can be easily made, where such is required.

$A_1 \ldots A_{12}$ are twelve pyrites-burners for pyrites in pieces. The burner-gases pass through the flue-dust chambers B, an ascending gas-flue C, and a cast-iron pipe D, lined with fire-brick, into the

Glover tower E, and from this by pipes F_1 and F_2 into the first chamber G_1 in its upper part. They leave this chamber on the opposite side near the bottom through three pipes H_1, H_2, H_3, connected with a common pipe H, which ascends and introduces the gases into the second chamber G_2 near its top through pipes H_4, H_5, H_6. In the same way the gases issue from G_2, through I_1, I_2, I_3, ascend through I, and enter through I_4, I_5, I_6, into the third chamber G_3. The object of dividing the gases among three inlet- and outlet-pipes is to utilize the whole section of the chamber for the process and to avoid any dead corners.

From the third chamber the gases travel through the long pipe K, where they are cooled and dried, into the Gay-Lussac towers. At the lowest point of K the condensing water is discharged. The gases pass seriatim through the two towers L_1 and L_2 and issue from the latter into the atmosphere, unless it is preferred to pass them into a chimney, or, preferably, to draw them out by mechanical means.

The total cubic space of the chambers is about 310,000 cubic feet, which, according to the experience with ordinary chambers at the majority of German works, is required for the regular daily production of 20 tons H_2SO_4 in the shape of chamber-acid. [This is as nearly as possible $=$ 19 cubic feet per lb. of sulphur burned, and corresponds with the practice of the majority of English works; but much less space is required for a high-pressure work, comp. p. 468.]

The Glover tower in its lower half is packed with a network of bricks on edge, in its upper half with dishes. The first Gay-Lussac is packed with dishes, the second with coke.

Fig. 434 is a plan of the whole plant, the store-tanks below the chambers and above the towers being marked in dotted lines. Fig. 435 is a sectional elevation on the line A—B, through the dust-chamber, Glover tower, and first acid-chamber; fig. 436 is a sectional elevation C—D, through the pyrites-burners, showing one of the Gay-Lussacs and chamber G_3 in front elevation. Fig. 437 is a sectional elevation on line E—F through the chamber building.

The building for the vitriol-chambers is planned in an economical way, proved to be both cheap and efficient at the various works of the Rhenania Company. The chambers rest on brick pillars of such strength that they can be reduced to a small number and thus permit of properly utilizing the space below the chambers for various purposes. The space round the chambers themselves is cased in wood, and the roof is covered with roofing-felt, with a ventilating rider.

The plans do not show the steam-boilers; it is understood that the steam comes from a central plant through the 2-inch pipe M (figs. 434 and 435), from which branches $M_1 \ldots M_{10}$ $\frac{7}{8}$ inch wide inside carry the steam to the centre of the chamber-top. The ascending part of the steam-pipe is provided with a trap for the condensing water in its lowest point; the mains M above the chambers descend slightly towards the pipes M_{11} and M_{12}, which carry away the condensed water. [Comp. on feeding the chambers with water in the shape of spray, p. 536 *et seq.*]

The Glover tower is served by two acid-tanks R_1 and R_2, placed on its top, for nitrous vitriol and chamber-acid (from G_3). At its bottom the acid runs through two coolers S_1 and S_2 into tank R_5, from which it is lifted by pulsometer P_1 into tank R_4 which supplies the Gay-Lussac tower L_2. The weak nitrous vitriol issuing from the latter runs into R_6 and is lifted by pulsometer P_2 into R_3, in order to be enriched in tower L_1. From this it runs into R_7 and is pumped by pulsometer P_3 into R_1, serving for the Glover tower. R_2 on the same tower receives acid from chamber G_3 through pulsometer P_4.

Mr. Niedenführ has also furnished the following estimate of cost, based on his practical experience and on German prices in 1902. I translate his figures into English measures and money:—

I. *Ground-space,* 27,000 superficial feet		£2,500
II. *Building,* for burners 3,770 ,, ,,	£ 420	
,, for chambers, 14,500 ,, ,,		
Incl. brick pillars, wood casing for chambers, felt roof and chamber frame .	2,960	
Foundations and frames of towers.........	120	
Sundries, incl. boiler-shed	300	
	——	3,800
III. *Steam-boilers and machinery.*		
Steam-boilers 430 superficial feet heating surface, incl. brickwork &c.	300	
Air- and water-pumps	120	
Pipes for steam, air, and water	125	
Pulsometers, incl. erection and acid-pipes.	205	
	——	750
Carried forward		£7,050

	Brought forword		£7,050
IV.	*Pyrites-burners.*		
	12 lump-burners	£ 900	
	Dust-chambers, nitre-ovens, connection with Glover tower	225	
			1,125
V.	*Chambers and towers.*		
	240 tons lead, at 16*s* 6*d*. per cwt., incl. cost of burning and materials for same	3,900	
	Materials for packing Glover tower &c.	300	
	,, ,, ,, Gay-Lussac towers.	475	
	Sundries	325	
			5,000
VI.	Sundries (reserve)		1,325
			£14,500

For the *second* case (as explained p. 496), figures 438 to 443 give sketches of a set of chambers designed by Mr. H. H. Niedenführ, as embodying the *latest progress in the combination of chambers and towers.* This set is to suffice for burning 20 tons 48–50 per cent. pyrites in 24 hours. The pyrites is burned in fine Herreshoff furnaces, *a, a* (*cf.* p. 349), or in any other kind of pyrites-kiln or burner. The gases first pass through the dust-chamber *b, b,* then through the Glover tower *c,* into the lead chamber *d,* provided with air-cooling shafts (p. 477) and water-spray injectors (p. 537 *et seq.*). From here they pass through plate-tower *e,* containing 10 layers of 28 plates each, at a distance of 12 inches from layer to layer, then into another lead chamber *f,* followed by plate-tower *g,* with 10 layers of 24 plates each, 12 inches apart, and plate-tower *h,* with 12 layers of 24 plates, 12 inches apart; at last at the top into plate-tower *i,* containing 16 layers of 20 plates each, 8 inches distant. This tower they leave at the bottom by the long conduit *k,* which takes them to the first Gay-Lussac tower, containing 24 layers of 16 plates each, 4 inches distant; and this is followed by the coke Gay-Lussac tower *m,* a fan-blast being placed between these two towers.

The circulation of the acids is marked by arrows, but it is more clearly shown in fig. 443. The acid from the Glover tower *c* runs through an air- and water-cooler into tank R_1. A pulsometer, P, pumps it into tank R_6, fixed above the coke Gay-Lussac tower *m.* From this the acid runs to the bottom into tank R_2, is pumped by

	106,750	40
2. *Apparatus.*	francs.	cent.
Pyrites-burners	31,686	70
Glover tower	26,188	75
Chambers (4500 cub. metres = nearly 160,000 cubic feet)	74,131	80
Carried forward	132,007	25

	francs.	cent.
Brought forward	132,007	25
2 Gay Lussacs, 20 metres high	22,804	10
Exit-gas tube	6,157	15
Steam-pipes	4,541	25
Acid-tanks and acid-eggs	15,144	55
Tools	943	05
	181,597	35

3. *Steam-boilers and engines.*	francs.	cent.
2 steam-boilers and setting	21,267	60
1 air-pump and pipes	9,167	15
1 water-pump and pipes	7,114	55
1 fan-blast and driving-engine	3,192	50
	40,741	80
Grand total	329,089	55

This apparatus is capable of making 6000 tons of O.V. per annum with the "forced work" or "high-pressure style" frequently alluded to, viz. a chamber-space of only 11 or 12 cubic feet per lb. of sulphur burnt. This is made possible by the extraordinarily great size (and cost) of the nitre-recovery apparatus. If this had been made of the usual dimensions, the cost would have been about 38,000 frcs. less, but then the production, at the usual rate of 2·25 kg. per cubic metre (say about 21 cubic feet per lb. of sulphur), would have been only 3600 tons per annum.

On the arrangement of sulphuric-acid works in the United States interesting notes are contained in the papers of Falding ('Mineral Industry,' viii. p. 579, and ix. p. 617) and of Gilchrist (Journ. Soc. Chem. Ind. 1899, p. 459).

YIELDS AND COSTS OF SULPHURIC-ACID MANUFACTURE.

In calculating the cost of manufacturing sulphuric acid, we must take into account the following factors:—

Cost of sulphur (brimstone, pyrites, blende);
Consumption of nitrate;
Consumption of fuel;
Wages;
Wear and tear of apparatus;
Interest on capital, general expenses, &c.;
Yield of sulphuric acid.

We will, in the first place, inquire into the *consumption of nitre* and the *yield*. We are here met at the outset by the difficulty of comparing the statements from different sources, arising from different fundamental quantities being taken as the basis of the calculation. Some calculate all the sulphur contained in the charge, others only that portion which has actually been burnt, not taking into account the sulphur left in the cinders. The latter way of calculating is more rational in theory; but in practice it is often less useful than the former. For it is known with perfect accuracy how much pyrites, and how much sulphur contained in it, has been put into the burners; but as the percentage of sulphur in the cinders varies, it is not known precisely how much has been burnt. Besides, the question is not only how the chamber process itself works, but also how the burning has been done, on which the smaller or larger residue of sulphur in the cinders depends. It is different when the percentage of sulphur in the cinders is almost constant and altogether very slight, as in burning pure ores in shelf-burners; in this case it is indifferent which way of stating the results is adopted.

The *consumption of nitre* is stated sometimes in percentages of pure sodium nitrate, sometimes in percentages of commercial nitrate; and in the latter case either 95, 96, or 97 per cent. is assumed. Here also we have a source of uncertainty and divergence, although not of such importance as that just mentioned. To each part of sodium nitrate correspond 63·53 parts of N_2O_5 or 74·12 parts of NO_3H or 134·76 of nitric acid of 1·34 sp. gr. (at 15° C.), the strength usually employed in vitriol-works.

The worst confusion prevails regarding the calculation of the *yield of sulphuric acid*. Some state it in terms of chamber-acid of 50° Baumé (=106° Tw.), some as 60° Baumé (=144° Tw.), some as commercial 168° Tw. (=66° Baumé), some as real monohydrate; what is worse, the reduction upon these terms is made by very varying and, in part, quite erroneous tables (comp. p. 179); and frequently it is quite uncertain whether by "oil of vitriol" (O.V.) an acid of 93 to 94, or one of 96 to 98, or one of 100 per cent. SO_4H_2 is meant. In the following pages, so far as the sources permit, all statements will be reduced to the only rational term, that of monohydrate, SO_4H_2.

Frequently, at works where none of the sulphuric acid is sold, but the whole is used for making salt-cake, the yield is calculated indirectly, from the quantity of common salt decomposed by it, according to more or less arbitrary assumptions regarding the quantity of sulphuric acid consumed for decomposing a unit of salt. Thus several large manufacturers, working with open roasters, assume a consumption (and consequently a make) of 81·33 parts of SO_4H_2 to each 100 parts of common salt. Now, in muffle-furnaces (blind roasters) decidedly less sulphuric acid is consumed than in open roasters; and yet a large Alsatian maker, using blind roasters only, assumes a consumption of 74 per cent. of vitriol of 66° Baumé on the sulphate, $=85·8$ per cent. on the salt, or 80·8 per cent. of real SO_4H_2 on the salt, which is all but equal to the above-named figure. This proves the uncertainty of such bases of calculation.

Consistently, several English alkali-works have given up calculating the yield of sulphuric acid altogether; they only state the yield of salt-cake upon the pyrites burnt, or upon the sulphur contained therein. Of course, this way of calculating is only possible where no acid is sold or used for any other purpose than decomposing salt.

Often no mention is made whether that portion of the sulphuric acid employed for the *decomposition of nitre*, which leaves the factory in the shape of acid sulphate (nitre-cake), has been allowed for in the calculation. We specify this in the following accounts, wherever it can be done from the sources.

Of course the following enumeration does not contain all and every statement of the kind scattered in innumerable publications, but only so much as suffices for forming a good idea of the state of affairs, both in former and in recent times.

I. CONSUMPTION OF NITRE.

(Compare also the statements, pp. 467, 470, 472, 475.)

1. *For Brimstone-acid.*

(a) *Without Recovery of the Nitre-gas.*

To 100 parts of brimstone charged:—6 to 9 parts (Knapp, Chem. Technologie, 1866, i. pp. 2, 298); at least 6, sometimes 7½ parts (Schwarzenberg, *l. c.* p. 400); 6 to 8 parts (Payen, Précis, 1877, i. p. 322); 7 to 8 parts (Scheurer-Kestner, in Wurtz's Dict. de Chim. iii. p. 158); 8·9 parts (Stevenson and Williamson, in Richardson and Watts's Chem. Technol. iii. p. 318); 10 parts (Wright, Chem. News, xvi. p. 93). Most of the sulphur-burning works enumerated in the Official Alkali Report for 1885 consumed 9 or 10 parts.

(b) *Recovering the Nitre-gas.*

4 to 5 parts (Knapp, *l. c.*); 3 parts (Schwarzenberg, *l. c.* p. 401); 5 parts (Payen, *l. c.* p. 322); 3 to 4 parts (Scheurer-Kestner, *l. c.*); 3 parts (several American works visited by myself in 1890).

2. *For Pyrites-acid.*

(a) *Without Recovery of Nitre.*

At the Oker works in 1857, 14·4 parts; 1859 to 1863, 13·4 for 300 parts strong acid (Knapp, Kerl-Stohmann); for 100 sulphur charged in the shape of pyrites, 10 parts (Schwarzenberg, *l. c.* p. 432), 9 to 11 parts (Payen), 12 to 14 parts (Scheurer-Kestner). According to Wright (*l. c.*), in different works, with pyrites of 45 to 50 per cent. 8·5 parts, of 30 to 50 per cent. 10 to 12 parts, of 35 per cent. 12·5 parts; with a set of chambers in bad repair, in the first year 9·31, in the second 9·84, in the third 10·02 parts. According to Gossage (*ap.* Richardson and Watts, p. 317) 13·3 parts with 30 per cent. Irish pyrites. From my own experience, on an average, with pyrites of 40 to 44 per cent. 10·8 parts; in neighbouring works 10·5 parts with smalls, 9·4 with lumps. At some French works I was informed of a consumption of 1·5 to 1·97 kilog. nitre per 100 kilog. acid of 50° Baumé, equivalent to 2·9 to 3·8 kilog. per 100 kilog. pyrites of 44·4 per cent., or 6·5 to 8·5 kilog. per 100 kilog. of the sulphur contained therein. [This statement does not appear trustworthy, viz. too low, looking at the figures from the same source for working with a Gay-Lussac tower.] Naville's statements see below.

(b) *Recovering the Nitre-gas.*

For 100 sulphur in the pyrites:—5 parts (Schwarzenberg, *l. c.* p. 432); 7 parts (Payen, *l. c.* p. 322); 7 to 8 parts, less with higher towers (Scheurer-Kestner, *l. c.*); 3·8 parts (Glover). According to my own experience (with insufficient absorbing-space) 3·5 to 4·5 parts; but when the work was irregular, chambers out of repair, as much as 6 or even 7 parts. Neighbouring large works 3·5 parts. K. Walter guarantees 0·7 part of nitre to 100 parts acid of 66° Baumé = 2·04 parts to 100 sulphur in 44-per-cent. pyrites. At the Oker works in 1877, 3·75 to 4·5 parts per 100 sulphur were used with pyrites pretty rich in sulphur, 4·5 to 6 parts with mixed and galeniferous ores; in 1901 on the average 4·8 parts. In French works (same source as above), they use per 100 kilog. acid of 50° Baumé 0·9 to 1·24 kilog., per 100 pyrites 1·73 to 2·38, per 100 sulphur charged 3·85 to 5·37 kilog. of nitre. According to notes collected by myself in 1878:—in German works, 2·3 to 3·1 nitre per 100 sulphur; in the best English works, about 3 per cent. (exceptionally, as stated by Affleck, 2·2 per cent.; in Lancashire some large works use even 5 per cent., comp. the Table on p. 467); in French works, (with a Glover tower) 2·7 parts, (without) 4·2 to 4·7 parts to 100 sulphur charged.

The nitre used is always less in winter than in summer. As between nitric acid and solid nitre no difference worth mentioning can be established; if any thing, slightly less nitre is used in the solid form than as nitric acid, if not the acid itself, but the nitre from which it was originally made is taken as the basis of calculation, as it ought to be.

Notes collected during the last few years:—English works 2·5 to 3·5 per cent. At one works they asserted that the actual loss was only 15 lb. nitre per ton of pyrites, that is, less than 1·5 per cent. on the sulphur, with only 17 cub. ft. chamber-space, and a yield of 41½ cwt. 96 per cent. salt-cake.

A first-class German works with specially good absorbing-apparatus and 16 cub. ft. chamber-space:—1·8 to 2·2 per cent. $NaNO_3$ on sulphur burnt.

Pierron (Monit. Scient. 1900, p. 567) states as the consumption of nitre in France = 0·75 to 1·12 kg. per 100 H_2SO_4 (= 2·25 to 3·36 kil. $NaNO_3$ per 100 S) for pyrites; and 1·0 kg. for 100 H_2SO_4 with blende.

II. Yield of Sulphuric Acid, SO_4H_2.

(Theoretically 306·25 parts per 100 sulphur.)

1st. *From brimstone* (always upon the sulphur actually burnt). 290 to 300, on the average 296 (Knapp); 297 SO_4H_2 = 319·35 acid of 66° Baumé (Schwarzenberg); "usually 296 to 300; even the theoretical quantity has been obtained" (*sic*! Payen, i. p. 321); 290 to 300 (Scheurer-Kestner). At some American works visited by myself in 1890 the yield of acid was stated = 305 real H_2SO_4, which must be an error, attributable to wrong specific-gravity tables, &c.

2nd. *From pyrites.* At Oker, in 1857, 1 cwt. acid of 66° Baumé per 1·89 cwt. ore (Knapp); 1859–63, per 1·729 cwt. ore (Kerl-Stohmann); 1877, in the same place, 160 chamber-acid of 50° Baumé (106° Tw.) were obtained from 100 pyrites; from 100 rich copper-ores 140 to 150 parts of chamber-acid, from 100 "mixed ores" 90, from 100 ore mixed with galena 70 parts of chamber-acid. The residual sulphur in the cinders from pyrites (always containing galena) amounts to 6 per cent., from the other ores to 10–12 per cent. (Bräuning).

In four Belgian works, 1854 (Official Report), on 100 parts sulphur in the pyrites charged 242, 237, 259, 238 parts SO_4H_2. The same works in 1874 by improved arrangement had arrived at 87·81, 92·17, 85·50, 89·30, per cent. of the theoretical quantity, or 268·8, 282·4, 261·8, 273·5 SO_4H_2 per 100 S (Chandelon).

In the best French works (Schwarzenberg), on 100 sulphur in the pyrites charged, 259·7 SO_4H_2; on the sulphur really burnt, 283·43. Payen (*l. c.* p. 322) makes precisely the same statement, with the addition that *usually* from 100 kilog. 46-per-cent. pyrites 100 to 115 kilog. acid are obtained (=239·1 to 250 SO_4H_2 per 100 sulphur). According to Scheurer-Kestner (*l. c.*) there ought to be the same yield on the really burnt sulphur of pyrites as upon brimstone, viz. 290 to 300 parts. According to Wright, with rich Spanish pyrites 82 to 84 per cent. of the sulphur is obtained as acid; of the loss of 16 to 18 per cent., 4 or 5 per cent. is sulphur left in the cinders, and 12 or 14 per cent. other losses. This means a yield of 251 to 257·25 SO_4H_2 per 100 sulphur charged (evidently with insufficient chamber-space). An anonymous chemist (in the Chem. News, xiv. p. 22) states the yield from 30-per-cent. Irish pyrites=82 to 81·1 per cent. of the theoretical, inclusive of the sulphur in the cinders.

My own experience and reliable statements personally obtained by me from large factories (where, however, the acid made was mostly calculated from the salt decomposed) are as follows:—(*a*) 238·5 SO_4H_2 on the sulphur charged, with 40-per-cent. small pyrites burnt in muffle-furnaces; (*b*) 240 SO_4H_2, ditto, with 42-per-cent. lump ore: both without a Gay-Lussac tower. (*c*) 263·2 on sulphur charged (own experience), with Gay-Lussac tower, but the work being several times interrupted. (*d*) 272 to 275 ditto (own experience), with a Glover and a Gay-Lussac tower, the latter not large enough. (*e*) 276·4 on the sulphur charged, or

301·5 on the sulphur burnt (average result of a large, well-managed factory with Glover and Gay-Lussac towers). (*f*) a number of notes collected in 1878 from the best German and French works agree most remarkably to a yield of 270–272 SO_4H_2 on the sulphur charged, or 285 to 290 on sulphur burnt. In the warmer climates the yield, even with sufficient chamber-space, is always found somewhat less in summer than in winter, about 3 per cent.

The consumption of coals for chamber-steam is stated =16·3 kilog. per 100 kilog. SO_4H_2 as the average of eight French factories working without Glover towers; at an English works with Glover tower the coal used for the chambers and the air-pump amounted to 17·5 parts per 100 parts of SO_4H_2. At Stolberg (1902) only 8·5 parts of coal was used for the chambers and air-pump for 100 parts acid of spec. grav. 1·71, or 10·9 parts to 100 H_2SO_4. Other statements, partly above, partly below those just mentioned, will be found in the following calculations.

Naville (Lunge & Naville, 'Fabrication de la Soude,' i. p. 413) gives the following statements from French works, for periods before 1880:—

	Expended for 100 parts of H_2SO_4 produced.				H_2SO_4 produced:	
	Pyrites:		Nitre: parts.	Coals: parts.	for each 100 parts sulphur: parts.	per cubic metre in 24 hours.
	parts.	per cent. S.				
a…………	73	49·5	1·45	19·0	277	about 1·5
b…………	88·50	42·3	2·70	12·2	267	1·58
c…………	92	41	3·14	13	265·2	2·10
d…………	95·2	40	2·96	12	262·4	1·60
e…………	100	40	3·10	12	250	1·58
f…………	93	40	2·75	11–12	268·5	1·28

a. Shelf-burner, Gay-Lussac and Glover towers.

b. Oliver-Perret furnaces, no Gay-Lussac or Glover towers.

c. Ditto (notice the slightly inferior yield and greater waste of water, with somewhat less chamber-space).

d. Poor pyrites, small works, no Gay-Lussac or Glover tower. Average of a year.

e. Same works, during the hottest month.

f. Same works, when burning less pyrites in the same chamber-space as before.

Sorel remarks that the just-quoted statements of Naville's do not represent the present results obtained at the best French works. One apparatus at l'Oseraie during the first 10 months when the Glover and Gay-Lussac towers had to be supplied with acid, and all the chambers with nitre, yielded 143·3 H_2SO_4 for 100 parts of 50-per-cent. pyrites, with an expenditure of 1·03 kilog. nitre per 100 H_2SO_4, and an average make of 3·359 kilog. H_2SO_4 per cubic metre (that is, rather more than 14 cubic feet per lb. of sulphur burnt). At the end of the year the same apparatus made 4·128 kilog. per cubic metre (=only 11·5 cubic feet of chamber-space per lb. of sulphur burnt!); the yield was 148·81 kilog. H_2SO_4 per 100 kilog. 50-per-cent. pyrites, with 0·8 per cent. sulphur left in the cinders. This means 301·2 H_2SO_4 per 100 sulphur burnt, and 0·75 nitre per 100 H_2SO_4, or 2·26 commercial nitre per 100 sulphur burnt. These figures, which Sorel took from the books of the Saint-Gobain Company, are certainly in every respect astonishingly much better than anything I have heard of elsewhere from the best-managed works, let alone the remarkably small chamber-space, and I must confess that I do not understand the possibility of such results.

Kienlen (Monit. Scient. 1889, p. 1238) makes the following statements concerning the work done at the best French factories in the year 1889. With good pyrites and properly constructed apparatus, the yield on 100 parts of sulphur *burned* is 295 H_2SO_4. 100 parts of pyrites leave about 68 parts of cinders, with an average percentage of 1 per cent. sulphur. With Sain-Bel ore of 51·5-per-cent. S, 100 parts of pyrites will yield 2·95 × (51·5–0·68) = 150 parts of monohydrated sulphuric acid, corresponding to a yield of 291 H_2SO_4 on 100 S in the pyrites *charged*. There is thus a loss of 15·25 H_2SO_4, or 4·97 per cent., the sulphur being used up as follows :—

Recovered in the shape of H_2SO_4	95·03
Lost in the exit-gases	3·65
Lost in the cinders	1·32
	100·00

The consumption of nitrate of soda in the best works averages 0·90 for 100 monohydrate produced = 1·35 for 100 pyrites, or 2·60 for 100 sulphur charged. This is obtained even with "forced work," where 1 cubic metre of chamber-space is made to yield 3·5 or even 4 kilog. of H_2SO_4 in 24 hours.

I have been favoured by the firm of Ernst Güssefeldt, of Hamburg, with the originals of six years' returns of the acid-works at Hamburg and at Kastrup (near Copenhagen), with permission to publish the results. The following are the averages taken from the six years' returns (1884–1889), and they are very good examples of the way of stating the yields:—

A. *Hamburg works.*

Description of Pyrites: Rio Tinto.

Average quantity burnt per annum	2775·6	tons.
,, percentage of sulphur in pyrites	48·8	p. c.
,, quantity of sulphur in pyrites bought	1354·6	tons.
,, ,, acid 106° produced	6322·2	,,
The same reduced to real H_2SO_4	3948·2	,,
Sulphur contained in acid produced	1290·0	,,
,, lost	64·6	,,
Per cent. sulphur lost in cinders*	2·69	p. c.
,, ,, ,, chamber-process	2·03	,,
,, ,, lost altogether	4·71	,,
95 per cent. nitrate of soda consumed, total	50·9	tons.
Ditto, per cent. of sulphur	3·75	p. c.
Ditto, per cent. of acid 106° Tw.	0·80	,,
Real H_2SO_4 made per 100 pyrites	142·5	,,
,, ,, sulphur	291·9	,,

B. *Kastrup works.*

Pyrites burnt per annum (average)	1896·2	tons.
Sulphur in pyrites (average)	49·2	p. c.
,, ,, per annum (average)	932·8	tons.
Acid 106° produced per annum (average)	4215·2	,,
,, calculated into real H_2SO_4	2534·5	,,
Sulphur contained in acid produced	860·2	,,
,, lost altogether	71·9	,,
,, ,, in cinders	6·85	p. c.

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* The quantity of sulphur found in the cinders was from 2·8 to 4; there was 70 cinders assumed per 100 green ore.

Sulphur lost in chamber-process	0·90 p. c.
,, ,, total	7·75 ,,
95 per cent. nitrate consumed (average)	22·92 tons.
,, ,, per 100 sulphur	2·41 ,,
,, ,, ,, acid 106° Tw.	0·50 ,,
Real H_2SO_4 made per 100 sulphur	282·9 ,,
Coals used per annum (average)	309·4 ,,

The remark is added that the possible errors in stock-taking through inaccuracies of tables and so forth, taking them all as increasing the real yields, cannot possibly in the aggregate amount to more than 4 parts of H_2SO_4 per cent. of sulphur, so that, for instance, the *minimum* quantity really made at the Hamburg works, in lieu of 291·9, might be 288 per cent. of the sulphur.

Cause of the Losses in Manufacturing Sulphuric Acid.

The causes of the *loss of nitre* have been mentioned in detail, p. 706. They are (1) loss of nitre-gas carried into the outer air, (2) nitrogen compounds left in the chamber-acid, (3) nitre-gas reduced to N_2O or N.

The *loss of sulphuric acid itself* arises from the following causes:—

1. Incomplete combustion of the sulphur (loss in the cinders); this has also been spoken of before (p. 315). With brimstone this loss is not worth mentioning; with pyrites it is so much the greater the poorer the ores are, and besides it varies enormously according to the construction of the burners and the care with which they are worked, from 1 to 10 parts and more of sulphur per 100 pyrites, or from 2 to 30 per cent. of the total sulphur. A portion of the sulphur is sublimed, and is found in the connecting-pipes and in the acid itself, and is a clear loss.

2. Losses of SO_2 by leakages of burners, pipes, chambers, &c. By bad draught much loss may occur, since then, at the doors of the burners, nitre-ovens, &c., the gas continually blows outward. Bad pipe-joints, but especially chambers worn down too much, lead to great losses. I have seen chambers which, when ultimately stopped, presented in their interior the image of the starry sky from the innumerable holes in the top; and Wright (Chem. News, xvi. p. 93) has independently used the same simile. Many manufacturers

have no idea of the great loss which they suffer in this way, by allowing, from motives of ill-timed economy, a chamber to go on too long and trying to patch it up. Wright found in a chamber-system that went three years without repairs :—

	Nitre for 100 parts of sulphur burnt.	Cubic metres of chamber-space per kilog. of sulphur burnt per diem.	Practical yield (theoretical =100).
First year	9·31	1·150	81·5
Second year ...	9·84	1·073	75·4
Third year	10·02	1·017	68·4

3. Losses of SO_2 by *incomplete conversion into sulphuric acid.* Extremely little SO_2 can remain dissolved in chamber-acid if there is an excess of nitrous compounds present; the greater portion of any remaining SO_2 escapes from the chambers into the outer air. The reason of this may be irregularity of the process in general, want of nitre, insufficient chamber-space, insufficient draught, &c., as explained in detail previously. The losses from this source are nearly always much greater where the nitre is not recovered, for the reasons stated above. The very widely divergent statements respecting the yield of sulphuric acid are explained to a great extent from this cause alone.

Statements of Costs for the Manufacture of Sulphuric Acid.

1. *From Brimstone.*

(Older statements in the 2nd edition pp. 764 and 765.)

The following cost-sheet for brimstone-acid at an American works has been supplied to me from a thoroughly authentic source; it refers to the year 1888 :—

Brimstone, 1,637,127 lb.	$19,070·00
Nitre, 91,057 lb.	1,858·00
Sulphuric acid 60° B., 80,380 lb.	402·00
Labour for operating and repairs	2,096·81
Office expenses	3,100·00
Coal, 454 tons (at 2240 lb.)	463·00
Oil, tools, &c.	240·00
Repairing materials	688·00
Carried forward	$27,917·81

Brought forward	\$27,917·81
Depreciation of buildings, furnaces, and chambers, at 50 cts. per ton of acid produced	1,721·00
Ditto of machinery, boilers, &c., at 10 cts.	344·00
Insurance	775·00
Interest 6 per cent. on \$60,000	3,600·00
Ground-rent	204·00
	\$34,561 81

Sulphuric acid 60° Baumé produced 6,885,373 lb.
Cost of 100 lb. acid 60° Baumé .... 50·2 cents.

N.B.—The nitre-cake, having very little value in America, is not taken into account. The consumption of nitre at the above works was unusually high (5 per cent. on the sulphur), owing to the small size of the Gay-Lussac tower.

2. *From Pyrites.*

(Comp. statements referring to former periods in the 2nd edition p. 766 *et seq.*)

I have received the following altogether authentic account of the cost of making sulphuric acid at a first-class English alkali-works for the 12 months ending Dec. 31, 1889.

One ton of real O.V. (H_2SO_4), in the shape of acid of 148° Tw., required on the yearly average:—

	£	*s.*	*d.*
14·12 cwt. pyrites, at 11·8*s.* per ton	0	8	4·0
27·06 lb. nitre, at £9 9*s.* per ton	0	2	3·4
5·30 cwt. coals, at 5*s.*	0	1	3·9
Process wages	0	3	3·7
Repairs (incl. wages)	0	4	4·1
General expenses and salaries	0	2	1·0
Sundries	0	1	4·4
	£1	3	0·5

The pyrites used was Spanish ore, testing on an average 49·55 per cent. sulphur. The yield of real H_2SO_4 on the sulphur bought was = 286 per cent., on the sulphur burnt = exactly 300 per cent. (calculated by Kolb's table). The chamber-space was rather more than 16 cubic feet per lb. of sulphur.

For *France*, Sorel gives the following statements concerning the cost-price of acid of 50° B. (=160° Tw.) at l'Oseraie (comp. p. 935), in November 1885:—

	Quantities.		Price.	Amount.		Total.	
	Total.	Per 100 kil. acid.		Altogether.	Per 100 kil.	Altogether.	Per 100 kil.
	kil.		frcs.	frcs.	frcs.	frcs.	frcs.
Superintendence	......	......	......	285.00	0·03	1,484·70	0·16
Labour	......	......	......	1199·70	0·13		
Pyrites	374,550	42·00	26·00	9738·30	1·09	11,191·96	1·25
Nitric acid 36° B.	5,409	0·61	26·58	1455·66	0·16		
Coal	87,850	9·85	21·50	1888·75	0·22	1,888·75	0·22
Lighting	......	......	......	302·20	0·04	770·70	0·09
Sundries	......	......	......	30·00	„		
Work of strange machines	......	......	......	438·50	0·05		
Repairs	......	......	......	587·75	0·07	587·75	0·07
General and unforeseen expenses	......	......	......	631·00	0·07	631·00	0·07
Deduct:						16,554·86	1·86
Cinders sent out	258,500	28·98	3·00	775·50	0·09	775·50	0·09
Produced 891,821 kil. acid 50° B.						=15,779·36	1·77
Equal to 557,388 kil. H_2SO_4							=2·83

There was produced for 100 kil. 50 per cent. pyrites: 148·81 H_2SO_4.

Commercial nitrate expended per 100 H_2SO_4: 0·74.

„ „ „ „ 100 pyrites: 1·11.

To the above items of expenditure should be added the amortization of the plant, the cost of which is detailed on p. 935, taking the buildings per year at $\frac{1}{20}$ cost-price, furnaces, chambers, towers, &c. at $\frac{1}{10}$, steam-boilers and engines at $\frac{1}{5}$ cost-price, which comes to 31,647 francs per year in all, or 0·527 franc per 100 kils. H_2SO_4 for the first 4 years, 0·39 frc. from the 5th to the 9th year, 0·09 frc. from the 10th to the 20th year. (We cannot admit that the amortization should be calculated at such a low figure from the fifth year onward, as the depreciation of the furnaces, chambers, boilers, &c. must certainly be taken into account, and the "amortization" should include the sums necessary to provide for their renewal.)

The cost of *concentrated* acid is stated by Sorel as follows, starting from acid of 53° B. (=116° Tw.):—

			francs.
1390 kil. acid of 53° B. (=1490 of 50° B.).	@	f. 20·36	28·31
Sulphate of ammonia 10 kil.	@	330	3·30
Coal for firing 150 kil.	@	22	3·30
„ „ motive power (pumps)	@	30	0·66
Share of engine work			0·50
Labour			1·60
Repairs			0·60
Amortization of platinum stills			3·00
General expenses			0·50
Cost of 1000 kil. acid 93 p. c. H_2SO_4			41·77

This is understood for a production of 9 or 10 tons acid per day in two coupled platinum stills. The amortization of the buildings is not included.

In *Germany*, F. Curtius (the owner of a large vitriol-works at Duisburg, on the Rhine) discusses at length the cost of sulphuric-acid-making (Chemische Industrie, 1879, p. 187). His statements are of great interest, as they refer to old-established works whose produce of vitriol was almost entirely sold as such, whilst other figures frequently refer to works where all general expenses were charged to alkali. The following costs all refer to acid concentrated to 144° Tw. by steam-heat (comp. *suprà*, p. 828), exclusive of packages and transit. We give only the maxima, minima, and averages of the 14 years over which the figures range, viz. 1865 to 1878, in shillings per ton:—

	Minimum.	Maximum.	Averag
(1) Wages	5·36	8·48	6·55
(2) General expenses (Management, Insurance, Rates, Taxes, Lighting, Cartage)	3·40	4·73	4·23
(3) Office expenses (without commissions, &c.)	1·98	2·77	2·32
(4) Repairs	3·31	9·31	5·93
(5) Amortization of plant (4 per cent. on old, 10 per cent. on new plant)	2·24	3·72	2·83
(6) Interest on capital	3·11	4·25	3·56
Total	19·40	33·26	25·42
Extra expenses for new plant	......	6·63	1·61
Annual working-days	304·4	352·4	329·40

If the acid had to be sent out in glass carboys, which were returned by the buyer, this caused an expense of 4*s*. to 6*s*. per ton; but sending it out in copper or lead vessels cost only from 0·6 to 1*s*. per ton for repairs, &c., of course exclusive of carriage.

Most of the above-stated items appear to be excessively high. As their *bona fides* cannot be doubted, they point to the fact that the process was not carried on in the most economical manner. This becomes almost certain by the following statement, which I have received from the most authentic possible source. It refers to an old-established German works and to the year 1889. (The "Mark" may be taken as slightly less than a shilling.)

Cost of 1000 *kilog.* (*=a ton*) *of real* H_2SO_4 *in the shape of acid of* 142° Tw.

702 kil. pyrites 47 per cent. at M. 1½ per 100 kil.=	Marks 10·53
13·1 „ nitrate of soda at M. 20	2·62
132 „ coals at M. 1	1·32
Wages for process	3·36
Repairs of buildings and apparatus	1·81
General expenses and management	2·56
	22·20

This does not comprise amortization of the plant, for which about 3 M. per ton must be charged, making the total=M.25·20, or rather less than 25*s*. per ton of H_2SO_4, exclusive of packages.

For Germany, Niedenführ and Lüty in 1902 (Zsch. ang. Ch. 1902, p. 242) give the following figures, referring to a plant producing acid equal to 20 tons real H_2SO_4 in 24 hours. When working with 50 per cent. Portuguese pyrites, 94·5 per cent. of the sulphur is utilized, 3½ per cent. being left in the cinders and 2 per cent. being lost in the chamber-process. Reckoning 2 Marks per 100 kil. of pyrites (after deducting the value of the cinders), the cost of sulphur for 100 kil. H_2SO_4 in the shape of chamber-acid is = M. 1·28. The consumption of nitric acid 36° B. with proper work is 1·1 part to 100 H_2SO_4, or at a price of 19 M. per 100 kil. = 0·21 M.; coals, 12 parts at 16 M. = 0·19 M. per 100 H_2SO_4. The labour is: 2 men for the steam-boilers, 3 men for moving the raw materials and cinders &c., 8 men for pyrites-burners, 2 men for the chambers (the acid being automatically pumped); altogether 15 men at 3 Marks = 45 Marks or 0·225 M. per 100 kil. [Both the number of men and the wages are reckoned rather low.]

When employing mechanical dust-burners (p. 349) the wages for 100 kil. H_2SO_4 decrease to 0·165 M., repairs 0·14 M. General expenses are not enumerated, as the calculation in question is to serve for a comparison of a cost of acid made by the chamber-process and such made by the contact-process; but this refers only to management, rates, taxes, insurance, &c., while the figure for amortization and interest is of paramount importance in that respect.

Amortization, in the case of sulphuric-acid works on the ordinary chamber-system, as erected in Germany during the last 20 years, may be reckoned on the basis of the following cost of plant for works turning out 20 tons H_2SO_4 per day *:—

	Marks.
Ground-space 2500 sq. met. @ 20 M.	50,000
Buildings	100,000
Steam-boilers and engines	16,000
Pyrites-kilns and gas-flues	48,000
Glover chambers and Gay-Lussac	156,000
	370,000

Assuming 7½ per cent. average amortization on plant, and 5 per cent. interest on total cost, that means 42,000 M. per annum, or per 100 kil. H_2SO_4 0·583 M. for amortization and interest. Where the plant is not constructed on rational and economical principles, this figure will be certainly exceeded and in reality in many practical cases reaches 0·75 M. and upwards.

This shows the very great importance of saving in the first cost

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* This estimate differs from that which Mr. Niedenführ has made of the plant shown in figs. 434 to 437 (p. 931) in several respects. The last-mentioned estimate applies to a cheaper kind of chamber-building, to lump-burners in lieu of smalls'-furnaces, and to a larger chamber-space than Mr. Niedenführ thought necessary in his latest estimate.

of plant, not in the wrong directions, but by increasing the yield of a certain cube of chamber-space by means of larger and better packed Glover and Gay-Lussac towers, by properly constructing the gas-flues, and, where necessary, applying mechanical means with a view to good draught, and principally by replacing part of the chambers by more energetically acting apparatus (pp. 471 *et seq.*), which promote better contact and better cooling of the gases, vapours, and misty particles. The principles for applying such "reaction-towers" are explained pp. 492 *et seq.*

We have also shown on p. 934 how Niedenführ plans a rational chamber-system on that principle. The cost of such a combination of chambers and towers would be (for 20 tons H_2SO_4 per diem):—

	Marks.
Ground-space 1850 sq. met. @ 20 M.	37,000
Buildings	34,000
Steam-boilers and engines	16,000
Mechanical pyrites-burners and flues	50,000
Chambers and towers	98,000
	235,000

Reckoning 7½ per cent. amortization on plant and 5 per cent. interest for plant and ground-space, we arrive at a sum of 26,600 Marks = 0·37 M. per 100 kil. H_2SO_4.

With a [hypothetical] system consisting of towers only, as sketched p. 494, Niedenführ reckons the total cost of plant and ground-space at 84,000 Marks, for a production of 7200 kil. H_2SO_4. This is = 0·384 M. amortization and interest per 100 kil. H_2SO_4, and shows that this part of the costs is practically no higher than the last calculated figure even for such a small factory (producing 7 tons H_2SO_4 per day) when working entirely without chambers. [This part of the calculation is not, like the remainder, based on actual experience.]

Niedenführ now gives the following synopsis (founded on actual observations and at the date above mentioned) of the cost of 100 kil. H_2SO_4 in the shape of chamber-acid or Glover-tower acid, without the cost of management &c.:—

	Older system, Chambers only, hand-worked burners. Marks.	Combination of Chambers & Lunge towers, mechanical pyrites-burners. Marks.
Pyrites	1·28	1·28
Nitric acid	0·21	0·21
Coals	0·19	0·19
Wages	0·225	0·165
Repairs	0·14	0·12
Amortization and interest	0·583–0·70	0·37
	2·628–2·745	2·335

With the figures thus found Niedenführ and Lüty compare those referring to the *contact-process*. They reckon the cost of a contact-plant for 20 tons H_2SO_4 per diem = 400,000 M., of which 37,000 M. are for ground-space. At 5 per cent. capital interest and 7½ p. c. amortization on plant this is = 0·67 M. per 100 kil. H_2SO_4. The royalties vary from 75,000 to 150,000 Marks = 0·104 to 0·209 M. per 100 kil. H_2SO_4. The cost of pyrites = 1·28 M. as before. Coals, according to various reports, are assumed to average 22 parts per 100 H_2SO_4, or at 16 Marks per ton = 0·352 M. per 100 kil. The wages must be rather higher, say 0·195 M. to 0·255 M.; repairs no less than in the case of chambers. Thus the authors arrive at a cost of from 2·529 to 2·996 Marks per 100 kil. H_2SO_4 made by the contact-process, which is essentially higher than the figures found previously for acid made by the old process. [It must be noticed that the latter estimates, but not the former, are based upon N. & L.'s own experience.]

The above refers to acid up to the strength of Glover-tower acid. The case is very different when *stronger acids* are required; in the case of the contact-process the cost is exactly the same per 100 H_2SO_4, but in that of the old process the cost of concentration must be taken into consideration.

For producing 20 tons H_2SO_4 in the shape of 93 per cent. acid, the cost of a platinum concentrating-plant, inclusive of buildings and lead pans, varies between 140,000 and 260,000 Marks. Apart from the loss of platinum (which in the case of Heraeus's platinum-gold apparatus, p. 877, is from 0·23 to 0·30 M. per 20 tons), we must reckon 5 per cent. interest, and with cheaper (but more hard-worked) apparatus 3 per cent., with dearer apparatus 1½ per cent.

amortization, which together amount to a minimum of 29·20 and a maximum of 47 Marks per 20 tons. From this, and taking as a basis the above-calculated cost of 2·335 Marks per 100 kil. H_2SO_4 in the shape of chamber-acid [comp. p. 953, taking the more favourable figure, as brought out by utilizing all rational improvements !], Niedenführ, and Lüty make the following calculations :—

	Maximum cost. Marks.	Minimum cost. Marks.
20,000 kil. H_2SO_4 @ 2·335 M.	467	467
3,600 kil. coals @ 16 M. per ton	—	57·60
or 4,400 „ „ „ „	70·40	—
4 men at 3 Marks	12	12
Loss of platinum (in case of Heraeus metal)	0·30	0·23
Repairs	10	7·50
Interest and amortization	47	29·20
21,440 kil. acid of 93 per cent.	606·70	573·53
100 „ „ „	2·83 to	2·67

This shows that, with large-sized platinum apparatus the expense is decidedly greater, although they suffer less than smaller apparatus.

Cast-iron concentrating-apparatus requires much more fuel (up to 50 per cent.), more labour, more repairs, and much more amortization (10 per cent.), so that the total cost of acid is always much higher than with platinum apparatus. But it is quite different with Kessler furnaces (p. 903), especially when combined with lead pans heated by the flues of pyrites-burners (p. 823). This plant costs only 35,000 Marks per 20 tons H_2SO_4, inclusive of buildings, and from this Niedenführ and Lüty derive the following calculation :—

	Marks.
20,000 kil. H_2SO_4 as chamber-acid @ 2·335 M.	467
2,000 kil. coke @ M. 16	32
1,200 „ coal @ 16	19·20
4 men @ 3 M.	12
Repairs (from practical figures)	6
Amortization and interest 15 p. c. on 35,000 M.	14·60
21,441 kil. 93 per cent. acid	550·80
100 „ „ „ „	2·57

Up to 96 per cent. acid Kessler apparatus can be used as well. For acid up to 98 per cent. Heraeus stills should be used, and the costs would be:—

	Marks.
20,000 kil. H_2SO_4 as chamber-acid	467
5800 kil. coal @ 16 M.	92·80
6 men @ 3 M.	18
Loss of platinum	0·45
Repairs	20
8 p. c. interest and amortization on 380,000 M.	62·22
2,050 kil. 97–98 per cent. acid	660·47
100 „ „ „ „ „	3·22

The same acid made by the contact-process would cost for 93 per cent., 2·35–2·79 M., for 97/98 per cent., 2·47–2·93 M. (in each case exclusive of management &c.).

The following table gives a synopsis of the above calculation of costs (in Marks) of 100 kil. concentrated acid:—

(*a*) 93 per cent. H_2SO_4.

Made in a platinum-gold still.		Made in a Kessler furnace.	Made by the contact-process.	
minimum.	maximum.		minimum.	maximum.
2·67	2·83	2·57	2·35	2·79

(*b*) 97/98 per cent. H_2SO_4.

Made in a platinum-gold still.	Made by the contact-process.	
	minimum.	maximum.
3·21	2·56	2·93

From this Niedenführ and Lüty draw the following conclusions:—

For the manufacture of acid of 50° to 60° B. (*i. e.* up to 78 per cent. H_2SO_4) a rationally constructed system on the old process is more advantageous than the contact-process.

For acid of 93 per cent. the contact-process is more favourable than the old system with concentration in platinum, but it balances the old system with Kessler furnaces.

For acids of higher strengths the contact-process has a decided advantage over the platinum concentration, whether combined with cast-iron apparatus or not.

Lastly, Niedenführ & Lüty make the following remarks:—As chamber-acid, made by plant erected on modern principles, is decidedly cheaper than acid of 50° B. made from anhydride, and the advantage of the contact-process comes in only with stronger acids, *that strong acid must be cheapest which is made by dissolving* SO_3 *made by the contact-process in chamber-acid or in acid concentrated to* 60° B. *by means of lead pans placed on the pyrites-burners.* For this they give the following calculations:—

	Minimum. M.	Maximum. M.
100 kil. 93 per cent. acid requires:		
33·6 kil. SO_3=41 H_2SO_4 @ 2·529	1·037	—
,, ,, ,, ,, @ 2·996	—	1·224
66·4 kil. acid 60° B.=51·8 H_2SO_4 made by the chamber-process @ 2·335	1·209	1·209
100 kil. acid 93 per cent. costs from	2·246 to	2·433

This means that manufacturers, under present circumstances, ought to keep up their chamber sets, with the necessary improvements (towers &c.), and make only so much SO_3 by contact-processes as is required to bring up the chamber-acid to the necessary strength. This, of course, in the first instance presupposes the employment of all rational improvements in the shape of first-class Glover and Gay-Lussac towers, plate-towers for part of the process, fan-blasts where necessary, &c.; and, secondly, it is only applicable for a somewhat large output. For smaller plants the combination of the chamber- and contact-process will not pay, and here the Kessler furnace comes in very well; or else several small makers might combine to start a common anhydride plant.

For *America* the following calculations of the cost-price of pyrites-acid is given in the United States 'Mineral Resources' for 1886, p. 671:—

2½ short tons of pyrites (46 per cent.), at 10 cents per unit per ton	$11·50
60 pounds nitrate of soda, at 2½ cents	1·50
5 cwt. of coal, at $4 per ton	1·00
Wages	3·00
Superintendence and management	2·00
General jobbing repairs	0·60
Interest on capital of $100,000 at 10 per cent.	6·15
	$25·75
Produce 4½ tons of 50° Baumé, cost per ton	$5·50

Stahl (Zsch. f. angew. Chem. 1893, p. 54) quotes the cost of producing chamber-acid of 50° Bé. in the east of the United States as follows (in bulk):—

A. *From Brimstone.*

2·5 tons brimstone (5600 lb.) at $21	$52·50
225 lb. nitrate of soda	4·50
200 lb. sulphuric acid 60° Bé. at $0·40	0·88
4 men, including firemen	6·00
Wear and tear of burners, chambers, buildings	5·40
Repairs	2·70
Coals, lighting, &c.	2·00
Management	5·00
Capital interest	5·00
13·5 tons chamber-acid cost	$83·98
1 ton „ „	6·22

B. *From Pyrites.*

5·5 tons pyrites (37 per cent. avail. sulphur) at $6	$33·00
180 lb. nitrate of soda	3·60
250 lb. sulphuric acid 60° Bé.	1·00
Breaking pyrites and removing cinders	1·40
6 men, including firemen	9·00
Wear and tear of burners, buildings, chambers	5·50
Repairs	2·75
Coals, lighting, &c.	2·00
Management	5·00
Capital interest	5·50
11 tons chamber-acid cost	$68·75
1 ton „ „	6·25

The purification from arsenic, if there is very little present, costs 10 cents per ton.

Hence the costs are about the same, if a ton of pyrites with 37 per cent. available sulphur costs $6·00, that is $16·20 for the sulphur contained therein, against $21 for Sicilian sulphur. The difference of $4·80 represents the lower value of available pyrites sulphur in comparison with Sicilian brimstone. In the case of

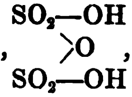
Spanish or other pyrites rich in arsenic, the difference in value must be taken=\$1·50 more, or=\$6·30. If, for instance, such pyrites with 47 per cent. sulphur costs \$8, the sulphur therein cost \$17·00 per ton, and this is the equivalent of a price of \$23·30 for Sicilian sulphur.

From comparative tables which William Wilke, M.E., and Dr. H. P. Weidig, of Newark, have drawn up, for the cost of producing sulphuric acid from pyrites or sulphur, I quote, with their permission, the following figures, choosing a medium plant for producing 10,000 tons of sulphuric acid per annum (evidently chamber-acid of about 50° Bé. is meant):—

	PYRITES.		SULPHUR.	
1 Glover tower	12×12×25 ft.		1 : 12×12×25 ft.	
2 Gay-Lussacs	6×35 ft.		2 : 6×35 ft.	
32 furnaces	5 ft. kilns.		1 : 16×20 ft. furnace.	
Cost of whole plant (frame buildings)	58,000 \$		50,000 \$	
Cost of whole plant (brick buildings)	73,000 \$		62,000 \$	
Pyrites 49 % avail. S @ 7 \$ (long ton)	3776·68 tons.	26436 \$		
Sulphur @ 17 \$ per 2000 lb.			2075 tons	35,275 \$
Nitre @ 2 c. per lb.		1660 „		1660 „
Coal for air and steam		2400 „		1800 „
Total cost of material		30,496 „		38,735 „
Labour: 1 manager		1500 „		1500 „
„ chambermen		(2) 1400 „		(2) 1400 „
„ furnacemen		(4) 2200 „		(2) 1100 „
„ labourers		(4) 1600 „		(1) 400 „
Total cost of labour		6700 „		4400 „
Repairs		1000 „		700 „
Interest 6 % on plant and working expenses		6180 „		6000 „
Insurance, taxes, water, and office expenses		6342 „		6200 „
Depreciation of plant		(2%) 1300 „		(1½ %) 1120 „
Total cost of yearly output		50,718 „		56,035 „
„ per ton acid		5·07 „		5·60 „

CHAPTER XI.

THE MANUFACTURE OF NORDHAUSEN OR FUMING OIL OF VITRIOL, AND OF SULPHURIC ANHYDRIDE.

ON pp. 165 *et seq.* the fuming or "Nordhausen" oil of vitriol has been described, and has been characterized as a mixture of sulphuric hydrate and pyrosulphuric acid,  $\begin{array}{l} SO_2-OH \\ \quad >O \\ SO_2-OH \end{array}$, a compound which has lately come into the market as "solid oil of vitriol."

Although in all probability fuming oil of vitriol is precisely that kind of sulphuric acid which was obtained first of all, and although about 1850 it was still manufactured in several places, and especially near Nordhausen, in Prussian Saxony, later on its manufacture according to the only method formerly employed was carried on exclusively in Bohemia, by the firm of Johann David Starck. The reason of this was that in this manufacture manual labour constitutes a very large portion of the expense, and that it requires a very large space and a great number of small apparatus, so that it can only pay under certain conditions rarely present. Owing to this, all other factories ceased to work, even those in the Harz (which, by the way, were not located at Nordhausen itself, where there was only a warehouse for the acid, but at Braunlage and Goslar).

So long as fuming oil of vitriol was only used for dissolving indigo (for which purpose it is very little employed now), the monopoly of the Bohemian firm was not very much felt; but since very large quantities of fuming acid were required in the mineral-oil industry, especially in the manufacture of alizarine and many other coal-tar

colours, many efforts have been made to produce that acid in another way; and success has at last been attained. The attempt was made in two ways:—first, by trying whether the ferric sulphate obtained by the Bohemian method cannot be replaced by other sulphates yielding their acid on heating, partly or entirely, as anhydride; and, secondly, trying whether the anhydride, or its solution in sulphuric hydrate cannot be obtained synthetically.

We shall, in the first place, describe the method by which the oil of vitriol was formerly exclusively obtained—namely, from "vitriol-stone"—which rests on the fact that ferric sulphate, $Fe_2(SO_4)_3$, at a red heat splits up into ferric oxide (Fe_2O_3) and sulphuric anhydride ($3SO_3$), the latter of which is partly decomposed into SO_2 and O.

The Manufacture of Fuming Oil of Vitriol in Bohemia.

All former descriptions of this manufacture have been rendered obsolete by that given by E. V. Jahn in Wagner's 'Jahresbericht,' 1873, p. 220. We shall give an abstract of the latter, adding some supplementary notes *.

The basis of the whole manufacture consists of certain slates, which contain from 1 to 31 per cent. of pyrites and are distinguished from ordinary roofing-slates by their darker colour and high specific gravity; analyses of these "vitriol-slates" are given in our second edition p. 836. The oxidability of these slates has led to a special industry, which has existed since the 16th century. When rich in alumina (which is only exceptional), the slates serve for making alum; when poor in alumina and rich in pyrites, for copperas and "vitriol-stone" (*Vitriolstein*), *i. e.* ferric sulphate—from which naturally followed the manufacture of fuming oil of vitriol. The Pilsen sulphur-works are already mentioned in 1526. The fuming oil of vitriol is the oldest form of sulphuric acid, and was first manufactured in Bohemia. The thirty years' war destroyed that industry, which was transferred to the Nordhausen country, and returned to Bohemia only in 1778 on a small scale, since 1792 on a larger scale, when Johann David Starck

took it in hand, at first with the assistance of men obtained from the Nordhausen factories.

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* The present account is much shorter than that given in our second edition, p. 835 *et seq.*, the above industry having been discontinued.

The manufacture is carried on as follows :—The schist is broken up by stone-breaking machines, and tipped into large terrace-shaped heaps, leaving both horizontal and perpendicular air-channels. By means of a system of spouts water can be sprinkled all over the heaps. The process of oxidation by weathering lasts about three years; and very large heaps having been made at first, strong lyes are always obtained. The ores, on lying in the moist air, become hot; the pyrites is oxidized, first to ferrous sulphate, then to ferric sulphate, along with a little aluminium sulphate. These salts, together with the pre-existing soluble salts, are lixiviated by water conveyed in the above-mentioned spouts. The brown liquors, possessing a density of generally 28°, and up to 38° Tw., are run into wooden reservoirs, where they remain some time for settling and are a little concentrated by spontaneous evaporation and also more highly oxidized. Then they are concentrated, by top-heat in brick-furnaces, up to 77° Tw.; the soot and ashes are allowed to deposit in settling-tanks; and the clear liquor is further evaporated in cast-iron boilers to a syrupy consistence. If then run on to the floor, it solidifies to "*crude vitriol-stone.*" This is a hard, pale green or yellowish-green mass, containing still a good deal of ferrous sulphate and water of crystallization. In order to remove the latter and to oxidize the former, it is calcined in open roasters. The *calcined vitriol-stone* is essentially anhydrous ferric sulphate; it is yellowish white, dissolves in water with a reddish-yellow colour without leaving any large residue; and the solution has a strongly acid reaction. It still contains a little ferrous sulphate and constantly, in variable quantities, aluminium sulphate along with a little magnesium and calcium sulphates. It takes from 6 to 20 tons of schist to make one ton of vitriol-stone. The stone formerly yielded only about 33 per cent. of "oleum"; later on, however, owing to improved processes, the yield was from 40 to 50 per cent.

The vitriol-stone is distilled in four works, altogether with 120 "oleum-furnaces." These are the well-known galley-furnaces, shown in our second edition p. 840. The calcined vitriol-stone is broken by crushing-rollers and charged into retorts made of fire-clay. On each side of the galley-furnace there are four tiers of

colours, many efforts have been made to produce that acid in another way; and success has at last been attained. The attempt was made in two ways:—first, by trying whether the ferric sulphate obtained by the Bohemian method cannot be replaced by other sulphates yielding their acid on heating, partly or entirely, as anhydride; and, secondly, trying whether the anhydride, or its solution in sulphuric hydrate cannot be obtained synthetically.

We shall, in the first place, describe the method by which the oil of vitriol was formerly exclusively obtained—namely, from "vitriol-stone"—which rests on the fact that ferric sulphate, $Fe_2(SO_4)_3$, at a red heat splits up into ferric oxide (Fe_2O_3) and sulphuric anhydride ($3SO_3$), the latter of which is partly decomposed into SO_2 and O.

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We shall, in the first place, describe the method by which the oil of vitriol was formerly exclusively obtained—namely, from "vitriol-stone"—which rests on the fact that ferric sulphate, $Fe_2(SO_4)_3$, at a red heat splits up into ferric oxide (Fe_2O_3) and sulphuric anhydride ($3SO_3$), the latter of which is partly decomposed into SO_2 and O.

The Manufacture of Fuming Oil of Vitriol in Bohemia.

All former descriptions of this manufacture have been rendered obsolete by that given by E. V. Jahn in Wagner's 'Jahresbericht,' 1873, p. 220. We shall give an abstract of the latter, adding some supplementary notes *.

The basis of the whole manufacture consists of certain slates, which contain from 1 to 31 per cent. of pyrites and are distinguished from ordinary roofing-slates by their darker colour and high specific gravity; analyses of these "vitriol-slates" are given in our second edition p. 836. The oxidability of these slates has led to a special industry, which has existed since the 16th century. When rich in alumina (which is only exceptional), the slates serve for making alum; when poor in alumina and rich in pyrites, for copperas and "vitriol-stone" (*Vitriolstein*), *i. e.* ferric sulphate—from which naturally followed the manufacture of fuming oil of vitriol. The Pilsen sulphur-works are already mentioned in 1526. The fuming oil of vitriol is the oldest form of sulphuric acid, and was first manufactured in Bohemia. The thirty years' war destroyed that industry, which was transferred to the Nordhausen country, and returned to Bohemia only in 1778 on a small scale, since 1792 on a larger scale, when Johann David Starck

took it in hand, at first with the assistance of men obtained from the Nordhausen factories.

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* The present account is much shorter than that given in our second edition, p. 835 *et seq.*, the above industry having been discontinued.

The manufacture is carried on as follows :—The schist is broken up by stone-breaking machines, and tipped into large terrace-shaped heaps, leaving both horizontal and perpendicular air-channels. By means of a system of spouts water can be sprinkled all over the heaps. The process of oxidation by weathering lasts about three years; and very large heaps having been made at first, strong lyes are always obtained. The ores, on lying in the moist air, become hot; the pyrites is oxidized, first to ferrous sulphate, then to ferric sulphate, along with a little aluminium sulphate. These salts, together with the pre-existing soluble salts, are lixiviated by water conveyed in the above-mentioned spouts. The brown liquors, possessing a density of generally 28°, and up to 38° Tw., are run into wooden reservoirs, where they remain some time for settling and are a little concentrated by spontaneous evaporation and also more highly oxidized. Then they are concentrated, by top-heat in brick-furnaces, up to 77° Tw.; the soot and ashes are allowed to deposit in settling-tanks; and the clear liquor is further evaporated in cast-iron boilers to a syrupy consistence. If then run on to the floor, it solidifies to "*crude vitriol-stone.*" This is a hard, pale green or yellowish-green mass, containing still a good deal of ferrous sulphate and water of crystallization. In order to remove the latter and to oxidize the former, it is calcined in open roasters. The *calcined vitriol-stone* is essentially anhydrous ferric sulphate; it is yellowish white, dissolves in water with a reddish-yellow colour without leaving any large residue; and the solution has a strongly acid reaction. It still contains a little ferrous sulphate and constantly, in variable quantities, aluminium sulphate along with a little magnesium and calcium sulphates. It takes from 6 to 20 tons of schist to make one ton of vitriol-stone. The stone formerly yielded only about 33 per cent. of "oleum"; later on, however, owing to improved processes, the yield was from 40 to 50 per cent.

The vitriol-stone is distilled in four works, altogether with 120 "oleum-furnaces." These are the well-known galley-furnaces, shown in our second edition p. 840. The calcined vitriol-stone is broken by crushing-rollers and charged into retorts made of fire-clay. On each side of the galley-furnace there are four tiers of

34 retorts each, the bottoms of those in the centre nearly touching each other. A fifth tier is formed at the top by 34 large retorts, open on both sides, reaching right across the furnace, and each side is provided with a receiver. Each of the smaller retorts also is connected with a receiver, large enough for holding the product of 4 or 5 distillations. The necks of the receivers are narrower than those of the retorts; they are put into the latter, and the joint plastered with clay. Such a furnace thus contains 272 small and 34 large oleum-retorts and 340 receivers. The lower part of the furnace, where the fireplace, grate, and ash-pit are located, is made of solid masonry; the upper part consists of a light arch, perforated for each retort in such a way that the necks of the retorts are held without any further support. The bottom tier of the receivers rests upon the brickwork, the higher tiers on wooden laths.

Into each retort is ladled, on the average, 750 grms. of vitriol-stone. The yearly consumption at Starck's works was 724,000 retorts and 40,000 receivers (previously twice as much). They are made at private potteries near the works, and thus cost only about 1*d.* to 1½*d.* apiece.

At the beginning of the distillation the temperature is slowly raised, so that after 4 hours the bottom tier of retorts has only attained a red-heat. During this time the retorts are left open; and consequently nearly all the ferrous sulphate still present is oxidized to ferric sulphate. With a higher heat aqueous vapour and sulphurous acid appear at the mouths of the retorts, generated from aluminium sulphate and still existing ferrous sulphate. Then thick vapours of sulphuric anhydride follow, which indicate the time for putting on the receivers. As the ferric sulphate simply splits up into Fe_2O_3 and SO_3, some liquid containing water must be put into the receivers, in order to condense and dissolve the sulphuric anhydride. This may be either rain-water or ordinary oil of vitriol. In the former case, ½ lb. of water should be put into each receiver, and it takes 4 or 5 distillations from the retort to attain the usual concentration of the oleum (79° Baumé). When the receivers have been charged with sulphuric acid of 66° Baumé (= 168° Tw.), it takes only 3 or 4 distillations to get it up to 80° Baumé.

When the oleum has reached sufficient concentration, which the workmen recognize from the speed with which a wood splinter, dipped into it, is charred, it is filled into stoneware bottles and left for a week to settle, after which time the clear acid is drawn off from the deposited mechanical impurities.

The ferric oxide remaining in the retorts (about 33½ per cent.) is known by the name of *caput mortuum*, *colcothar*, *English red*, &c. (In England a similar article is called "Venetian red.") It is raked out of the retorts after each distillation, and exhibits different colours according to the degree of heat to which it has been subjected. The lower tiers supply it of darker, the upper ones of lighter colour. In the crude state it was very difficult to sell as a common pigment or polishing-powder. J. D. Starck improved this article very much by proper treatment; so that in 1872 1000 tons of it were sold, of 19 shades and 41 grades, especially for painting ships. It is ground under French mill-stones and again calcined with the addition of common salt and at a certain temperature. The yellow shades are obtained by an addition of 2 per cent. of salt, igniting for an hour, and gradual cooling in a closed space; the brown shades, by adding 4 per cent. of salt; the purple shades, by 6 per cent. of salt, igniting for 6 hours at a gradually increasing heat, and rapid cooling. The igniting takes place in fireclay pipes lying in galley-furnaces similar to the oleum-furnaces, each of them containing 60 pipes. Unless the temperature is exactly regulated, the product becomes dark brown, and is then of little value. The best is contained in the two top tiers. After the igniting and cooling, it is sifted and levigated; by mixing the three above-named principal shades, the commercial shades between yellow, purplish red, and dark purple are obtained, which now only require drying and packing.

The smallness of the retorts used for decomposing the vitriol-stone, and the large number of these apparatus consequently necessary, are evidently to be explained by the fact that in larger apparatus the heat would penetrate too unequally and would cause great loss by overheating one part and insufficiently heating another part of the charge.

From Stolba (Fischer's Jahresb. 1885, p. 316) we will only quote the following analyses:—

1. *Vitriol-stone.*

Ferric sulphate	50·17
Aluminium sulphate	11·94
Ferrous "	1·35
Magnesium "	1·17
Calcium "	0·33
Copper "	0·20
Sodium "	0·11
Potassium "	0·13
Sulphuric acid	1·49
Silicic acid	9·10
Traces of Mn, As, P_2O_5	—
Water	23·31
	99·30

2. *Caput mortuum.*

Ferric oxide	74·62
Alumina	12·53
Magnesia	3·23
Lime	0·82
Sulphur trioxide	5·17
Silicic acid	1·17
Copper oxide	0·20
Water	1·30
	99·04

From a private source we can add that under the most favourable circumstances the yield from 100 parts of ferric sulphate, with 52 to 54 per cent. SO_3, is hardly 36 parts of sulphuric anhydride testing 95 to 96 per cent., which is, of course, dissolved in the acid contained in the receivers.

In 1792, one cwt. fuming oil of vitriol cost in Bohemia 50 fl. (say £5), in 1873, 10 fl. (£1); the production in 1832 was about 1000 tons, in 1846, 3000 tons, in 1873, 3360 tons, in 1884, 4350 tons. In 1900 the Bohemian manufacture from vitriol-stone was definitely abandoned.

The Production of Sulphuric Anhydride and Fuming Oil of Vitriol from artificially prepared Sulphates.

Two ways are possible for preparing SO_3 from sulphates, viz.: either employing such sulphates which split up at a sufficiently low temperature, or employing those compounds which stand midway between SO_3 and the sulphates—that is, pyrosulphates of the type

$$RO—SO_2—O—SO_2—OR.$$

The only representative of the former class is the *normal ferric sulphate,* $Fe_2(SO_4)_3$. Many other sulphates can be decomposed by heat, as those of aluminium, zinc, copper, &c.; but in all cases, except the first, the decomposition takes place only at temperatures at which SO_3 itself splits up into SO_2 and O. Thus, for instance, the $ZnSO_4$, so easily formed in roasting blende, on heating to a bright red-heat yields ZnO, SO_2, and O, but no SO_3. But ferric sulphate is already decomposed at a dark red-heat, scarcely visible in daylight, so that the SO_3 given off is not yet decomposed, and the reaction is simply:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

This reaction can never be realized to its full extent, as it is impossible to bring all the contents of the decomposing-apparatus exactly to the minimun temperature required; a considerable portion of the mass is too much heated, and, moreover, much of the SO_3 first formed is subsequently overheated in contact with hotter parts of the mixture or the walls of the apparatus, so that part of the SO_3 is always split up into SO_2 and O, and is thus lost, unless these gases are recombined by special means, viz. by the contact-process (comp. below).

Both this circumstance and the difficulty of preparing ferric sulphate cheaply enough have militated against the, apparently so easy, imitation of the Bohemian process, which consists in treating ferric oxide with strong sulphuric acid, heating the mixture till all the water has been driven off and dry ferric sulphate has been produced, and continuing the heating at a higher temperature, with condensation of the sulphuric anhydride evolved, the residue of ferric oxide serving over and over again for the same purpose.

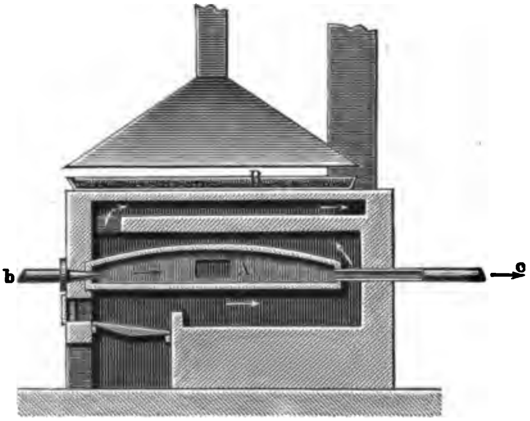
This process is much more difficult than it appears and was never successfully carried out.

An invention intended to improve the Bohemian process, but applicable also to sulphates prepared in other ways, and introducing already a "contact"-process, was made by R. Schuberth (G. P. 52,000, April 4, 1889). He states that the formation of sulphurous anhydride is the principal cause of the loss which, in the best case, amounts to 30 per cent. of the total SO_3, and in the case of large vessels or furnaces may destroy all the SO_3 present. This is caused by the prolonged contact of free SO_3 with the red-hot sides of the retorts; and this circumstance has hitherto confined the Bohemian process to the use of small vessels, involving a large consumption of fuel and of clay retorts, together with the necessity of employing much skilled labour and other drawbacks, such as the escape of acid smoke into the atmosphere. All this is avoided by bringing about the decomposition of the sulphates in a partial vacuum, and removing the vapours by aspiration. This can be done with ferric sulphate obtained in the Bohemian manner from schist, or with artificially prepared sulphates of iron &c. The operation is carried on in a horizontal shallow fireclay retort, provided with a cast-iron mouth-piece like that of gas-retorts. This mouth-piece contains an opening for charging and discharging, and a stirring-rake sliding in a stuffing-box; when not at work, the rake is pulled back towards the front so as to be out of the heated portion of the retort. Above the furnace is placed a cast-iron tube, containing a suitable filtering-substance for the gases, such as broken glass or pottery, asbestos, glass-wool, and the like. This gas-filter communicates on the one side with the retort, on the other side with a cast-iron air-pump. The vapours, drawn by this pump from the retort and passed through the filter, are forced through an upright cast-iron cylinder, lined with earthenware and containing a number of perforated dishes, charged with 10 per cent. platinized asbestos. The apparatus is heated by the waste gases from the retort-fire and serves for regenerating SO_3 from the small quantities of SO_2 and O formed in the retort. From here the vapours pass into cast-iron condensers, where they are absorbed by strong sulphuric acid, the condensation being aided by pressure. During the operation the sulphate within the retort is raked up several times; but while this is done, the pump is stopped in order to avoid any dust being drawn away. The employment of a vacuum causes a quick decomposition of the ferric sulphate, with but slight formation of SO_2; the duty performed by the apparatus is large, and the consumption of fuel much less than before. The residue is not overheated, as is the case in the lower ranges of the galley-furnace, and is thus better adapted for use as a paint; from the same reason it is also possible to use it over again for forming ferric sulphate. If sodium sulphate is to be used, the retort is made with a dished bottom, lined with platinum. This is charged with sodium sulphate once for all; by adding sulphuric acid of 140° Tw. bisulphate is formed, which (in the same way as is done in the case of ferric sulphate) is first heated without connection with the condensers till all the water has been driven out, and fumes of SO_3 and SO_2 appear, whereupon the connection is established and the heating continued. The residue in the retort is again treated with ordinary sulphuric acid, and thus used over and over again (comp. Neale's patent, *infrà* p. 992.).

I am not aware whether Schuberth's process has been practically carried out, and if so, with what success.

It is, however, possible that the following process may be profitable, since under the special circumstances of the case the acid costs nothing (or less than nothing, considering the trouble caused by the necessity of removing it), and the value of fuel in the special local case is also extremely slight. Ragosine and Dworkowitsch (G. P. 43,453) employ the *acid-tar* (*sludge-acid*) produced in the purification of crude petroleum in enormous

Fig. 444.



quantities and containing up to 90 per cent. free acid. This they mix with ferric oxide. On mixing there is a strong reaction, so that part of the water evaporates; and sometimes even cooling is necessary, as the decomposition of the sulphate begins at 150° C. The solid mass produced is crushed and dried, and is heated to 300° or 500° C. Fig. 444 shows the furnace employed for this purpose. It consists of a muffle A with a very low arch; through the tuyere *b* dry air is injected, and the heavy vapours of sulphuric anhydride are drawn off through *c*. The waste fire-gases serve for drying the mass in pan B.

Some have proposed to make fuming O.V. from *ferrous sulphate* (copperas) which, on calcination, yields basic ferric sulphate, $Fe_2O(SO_4)_2$; but this is evidently even much less promising than the process starting with Fe_2O_3 and H_2SO_4, and the calculations made by Schemfil (French Patent, Dec. 2, 1869; Monit. Scient. 1870, p. 492) are entirely worthless.

Magnesium sulphate was patented by Sonstadt (March 3, 1875) in the shape of natural kieserite or calcined Epsom salts. The operation was to be carried out exactly as with ferric sulphate. But it is a fact (comp. Wagner's Jahresb. 1876, p. 327) that magnesium sulphate on calcination yields very little SO_3, mostly SO_2 and O.

Sodium pyrosulphate, $Na_2S_2O_7$, is readily produced by heating the easily manufactured bisulphate, $NaHSO_4$, till the chemically combined water is expelled. On heating to a higher temperature the pyrosulphate itself gives off sulphuric anhydride, $Na_2S_2O_7 = Na_2SO_4 + SO_3$, and the normal sodium sulphate left behind can be employed for again making bisulphate. This has formed the basis of more than one proposal.

Prelier (Engl. Patent, June 29th, 1847) has proposed to prepare fuming oil of vitriol by the following process, which is said to have been carried out in France on a large scale, evidently only for a short time (if at all). 100 parts of calcined sodium sulphate are mixed with 2 parts of potassium sulphate and 2 parts of gypsum, charged into retorts of sandstone (?), and a sufficient quantity of concentrated sulphuric acid added to form bisulphates. Then heat is applied; first all the water distils over, then sulphuric acid of 77°, then of 106°, then of 170° Tw., and at last fuming acid. The latter is known by the drops falling into water producing a hissing noise;

then a receiver filled with acid of 170° Tw. is put on. This acid sometimes contains sodium sulphate. The residue in the retort is always used for the same purpose.

Wallace obtained an English patent (May 30, 1876) for heating sodium bisulphate in fireclay retorts; the formed anhydride or fuming vitriol is to be collected in earthenware jars with a lid perforated for receiving the gas-pipe, which can be replaced by a plain cover; thus the acid can be sent out in the receiver itself, and the fumes emitted in pouring it from one vessel into another are avoided. The fumes first coming over, which consist of aqueous sulphuric acid, are condensed separately. The sodium sulphate remains in the retort, and is always reconverted into bisulphate by adding sulphuric acid; so that continuous operation is possible.

Dr. Adolph Clemm (personal information) introduced the bisulphate process at the works of G. C. Zimmer at Mannheim in 1877, and already in May 1877 he delivered 80 stone jars of 40 per cent. fuming acid to the Badische Aniline and Soda works. This process was carried on for a number of years, until the adoption of the contact-process by the Badische and other factories made competition impossible.

Fuming Sulphuric Acid from the action of Boric Acid upon Sodium Bisulphate (Kerl-Stohmann, 'Chemie,' 3rd ed. vi. p. 156). —This method has probably never advanced beyond the state of a suggestion.

From Magnesium Sulphate and Sodium Pyrosulphate mixed.— Wolters obtained a German patent (No. 3110, March 5th, 1878) for this purpose. $MgSO_4$ acts upon $Na_2S_2O_7$ considerably below a red-heat, a double salt ($MgSO_4$, Na_2SO_4) being formed and SO_3 being liberated. Instead of Na_2SO_4, K_2SO_4 &c. may be employed. The remaining salt is reconverted into the mixture first employed by treatment with water and ordinary sulphuric acid, and exposing to sufficient heat. The value of this process is said to consist in the fact that the anhydride is liberated at a much lower temperature than from sodium pyrosulphate alone, thus preventing much loss, causing a larger yield of SO_3, and permitting the use of ordinary fire-proof materials without any extraordinary wear and tear. (Experiments made in my laboratory with Wolters's process have to a great extent confirmed these statements.)

An additional German patent (No. 6091, Oct. 13, 1878) contains a simplification which I in my laboratory experiments had employed as a matter of course. Instead of treating the residue from distillation with water and separating the salts by crystallization, the dry double salt ($Na—SO_4—Mg—SO_4—Na$) is ground and treated directly with sulphuric acid (1 equivalent to 2 of salt, as otherwise half the acid passes over in the hydrated state).

On the large scale Wolters's magnesium process does not seem to have been successful. But this appears to have been the case with a further process of his, patented in 1881 (G. P. 12,295). He prepares sodium pyrosulphate, in the usual manner, by heating the acid sulphate $NaHSO_4$ till the water has been expelled. When adding to the pyrosulphate a large quantity of monohydrated sulphuric acid there is a decomposition according to the formula :

$$Na_2S_2O_7 + H_2SO_4 = 2\ NaHSO_4 + SO_3.$$

The SO_3 is distilled off, and the hydrosodic sulphate is used for starting the process over again. This process has been actually at work in several factories, *e. g.* at Einergraben near Barmen during the years 1884 to 1889 (communication from Dr. Adolph Arndt).

A further patent of Wolters's (G. P. 15,639) shows that on heating a mixture of a pyrosulphate with concentrated sulphuric acid in cast-iron vessels a crust of iron sulphide is formed, which firmly adheres and resists the acid in the process of distillation so long as the hydrosodic sulphate remains in the retort.

A detailed study of the pyrosulphates has been made by H. Schulze (Ber. d. deutsch. chem. Ges. xvii. p. 2705); we can give only a very short abstract here. Dry potassium or sodium sulphate absorbs SO_3 at the ordinary temperature with considerable evolution of heat; but if a complete potassium pyrosulphate is to be formed, a higher temperature is necessary (soaking with SO_3 and distilling off the excess at 100° to 120°). The sodium salt, treated in this manner, contains only 85 per cent. $Na_2S_2O_7$. Many other bases form pyrosulphates as well. The method of Berzelius for preparing pyrosulphates, by heating the hydrosulphates, gave unsatisfactory results; a better result is obtained by heating sulphates with chlorosulphonic acid (employing an excess of this, which is afterwards distilled off), the reaction being:

$$K_2SO_4 + SO_3HCl = K_2S_2O_7 + HCl.$$

[Unfortunately chlorosulphonic acid has hitherto been prepared by means of SO_3, so that that process is not available for technical purposes.]

An excellent process for preparing sodium pyrosulphate is that of Baum (G. P. 40,696). 240 kilog. hydrosodic sulphate, or else 142 neutral sodium sulphate, and 98 kilog. monohydrated sulphuric acid are put into a cast-iron retort, provided with agitating-gear and connected with an air-pump. The latter is set in motion to produce a vacuum, and the retort is heated first to 260°, afterwards, with constant agitation for 5 to 8 hours, to 300° or 320°. Most of the water comes off between 260° and 280°, if the vacuum is equal to a column of 500 or 600 millim. mercury; the heating to 320° is only done to make quite sure of finishing the reaction. It is useful to place between the retort and the air-pump a cooler, connected by a glass tube with a receiver. When no more water is observed to run down the glass tube the reaction is finished, and the melted mass is poured out to solidify into plates consisting of pure $Na_2S_2O_7$ (comp. Schuberth's process, p. 966).

The Utilization of the Sulphuric Anhydride contained in Pyrites-kiln Gases.—It is well known that ordinary pyrites-kiln gases contain a somewhat considerable quantity of sulphuric anhydride, which may occasionally amount to nearly 10 per cent. of the total sulphur acids present (comp. p. 405). This fact has been utilized by various inventors. Majert and Messel (E. P. 1201, 1878) pass the burner-gas through concentrated sulphuric acid, which dissolves the SO_3, and can thus be brought up to real monohydrate, H_2SO_4, or even further; but undoubtedly this acid must be saturated with SO_2 as well, and this will make it useless for most purposes.

Dehydration of Sulphuric Acid by Metaphosphoric Acid.—Nobel and Fehrenbach (E. P. 10,860, of 1884) pass the vapours of boiling strong sulphuric acid over lumps of metaphosphoric acid heated to 320°. This acid retains the water and part of the sulphuric acid, whilst vapours of sulphuric anhydride are given off and are condensed in the usual manner. The operation is performed in a vessel of glass or platinum heated in a sand-bath, the sulphuric-acid vapours being passed in by a tube reaching nearly to the bottom. The vapours of SO_3 escape at the top, the liquefied mixture of phosphoric and sulphuric acid runs out at the bottom, and is reconverted into metaphosphoric acid by evaporation and calcination at a low red-heat. [Up to the present no material is known by which this process could be carried out. Glass or platinum certainly do *not* resist the action of fused phosphoric acid for any length of time.]

Sulphuric Anhydride from Chamber-crystals.—O. von Gruber (G. P. 27,726) proposed making SO_3 from nitrososulphuric acid (chamber-crystals) by heating them with dry air and sulphur dioxide at a higher temperature, and recovering the nitre gas evolved.

Application of Electricity for manufacturing Sulphuric Anhydride.—Léon (F. P. 206,088, June 9, 1890) proposes manufacturing sulphur trioxide by the electrolysis of sulphuric acid of 66° or 65°·5 Baumé. The current must not exceed $\frac{1}{10}$ ampère per square centimetre, in order to avoid heating. Thus SO_3, H, and O are produced; the former is condensed and the latter escape. The electrodes are made of platinum or carbon; they are kept 2 or 3 millimetres apart by means of asbestos or glass-wool, which reduces the electrical resistance of the bath to 2 or 3 ohms per centimetre, and permits a near approach to the theoretical yield, viz. 1 kilog. H_2SO_4 for each half horse-power per hour, or 1 kilog. of 45 per cent. Nordhausen acid. Sometimes a deposit of sulphur is formed on the cathode, but this is got rid of by reversing the current.

Some more details respecting Léon's process are given in his German patent (No. 57,118). He works in a cast-iron tank, cooled from without and covered with a slate slab. In the centre is the hollow platinum anode, with a water-cooled brass box inside. It is surrounded by an open, annular cathode, provided with open passages at the bottom, and supported by glass-coated copper rods, ending in platinum caps. With currents of very low density (0·1 amp. to 1 square centimetre), in which case the voltage can be lowered to 2·5, the electrodes are 3 centimetres high, and consist of crude copper, coated on both sides with platinum-foil soldered with gold; these are coiled in a spiral shape and kept at a proper distance by glass rods and asbestos cord. Per hour 1 kilog.

anhydrous acid [monohydrate ?] can be produced with an expenditure of 0·9 H.P., or 1 kilog. fuming acid of 68° Baumé with an expenditure of 1·2 H.P.

The Manufacture of Sulphuric Anhydride (also of Fuming and Ordinary Sulphuric Acid) by " Contact "-Processes.

This manufacture, which, after a number of unsuccessful attempts, made during a period of many years, was definitely established in the last quarter of the 19th Century, has during the last few years enormously increased in importance, and apart from supplying all the fuming sulphuric acid now used, bids fair to oust the time-honoured lead-chamber process, at least for the manufacture of highly concentrated acid.

Up to 1899 very little was known as to what the various factories were doing in that respect, complete secrecy being observed thereon. The ice was broken by the publication of the patents taken out almost simultaneously by the Badische Anilin und Sodafabrik, by the Hoechst works (Meister, Lucius, & Brüning), and the Mannheimer Verein chemischer Fabriken. But even then most of the circumstances of the rise and the present state of this industry remained unknown. This veil was to a certain extent lifted by a lecture given by Dr. Knietsch, of the Badische Anilin und Sodafabrik, before the German Chemical Society and published in the Berichte, 1901, vol. xxxiv. pp. 4069 *et seq.*

It is needless to say that I have fully drawn upon this source in my account, as well as upon everything else accessible in print; but I have had, moreover, the good fortune to receive, for the purpose of this work, extended and most valuable communications, embracing very many hitherto unpublished facts, from most of the firms or inventors connected with the new contact-processes, as will be apparent by the full quotations given from these in the following pages.

The first observation of what we now call "catalytic" or "contact" reactions, seems to have been made by Sir Humphrey Davy, in 1817. He found that heated platinum wire, introduced into a mixture of oxygen or air with hydrogen, carbon monoxide, ethylene, or cyanogen, increases its heat to a vivid glowing, and that the gaseous mixture is slowly or rapidly burned. In 1820

Edmund Davy found that platinum black, obtained by precipitating a platinum solution with hydrogen sulphide, treating the precipitate with nitric acid, evaporating the solution, and boiling the residue with alcohol, when moistened with spirit of wine, glows up in the air with combustion of the spirit. In 1822 Doebereiner found that the residue produced by igniting ammonio-platinum chloride, when moistened with alcohol, in the air behaves in the same manner; and in 1823 he found that finely divided platinum inflames a current of hydrogen, directed upon it in the presence of air, upon which reaction he founded, in 1824, his celebrated inflaming machine.

Although the terms "contact" or "catalytic" reactions were not used at that time, it is worthy of notice that, soon after Doebereiner had discovered what we now call the contact reaction of platinum in effecting the union of oxygen and hydrogen, Dulong, Thenard, and Dumas found that a number of other substances, both simple and composite, had the same effect; and the notion soon gained ground that these substances owe their function to their porous properties by which gases are condensed within the pores to a small volume, and the molecules are thus brought more nearly together, so that they can react more easily upon each other.

In 1835, Berzelius (Jahresbericht, xv., published in 1836, pp. 237 *et seq.*) comprised the just mentioned reactions in the same group with a number of reactions observed in organic chemistry (the conversion of starch into sugar by dilute acids, the fermentation of sugar by yeast, the production of ethylic ether from alcohol by strong sulphuric acid), also with the decomposition of hydrogen peroxide by a number of substances, all of them apparently caused by a certain body which remains unchanged and does not itself take part in the new combinations. Berzelius more especially refers to the celebrated investigations by Mitscherlich on the action of sulphuric acid in the formation of ether from alcohol; the terms "contact-substance" and "contact-reactions" indeed were first used by Mitscherlich. Berzelius, however, went further and attributed the above, and all analogous reactions, which he calls "catalyses," to a new "catalytic force" which he does not define very clearly.

We must here mention that Berzelius in the work just quoted does not refer to the contact action of platinum on the union of sulphur dioxide and oxygen, although this fact could hardly have been unknown to him. We shall enter into the general subject of catalysis later on.

Several years before Berzelius published the above generalization, a fundamental invention had been made which applied to what was afterwards called the catalytic action of platinum in the preparation of sulphur trioxide from dioxide and atmospheric air. A British patent No. 6096 (March 21, 1831), by Peregrine Phillips Junior, of Bristol, vinegar manufacturer, describes "Certain improvements in manufacturing sulphuric acid, commonly called oil of vitriol, viz., firstly, causing an instantaneous union of the sulphurous acid gas with the oxygen of the atmosphere, and so save saltpetre and the cost of vitriol chambers, by drawing them in proper proportions, by an air-pump or otherwise, through an ignited tube or tubes of platina, porcelain, or some material not acted on by heated sulphurous acid gas, in which are fine platina wire or platina in any finely divided state. The sulphuric acid formed is absorbed in a lead-lined tower, filled with pebbles over which water is made to trickle down."

Undoubtedly we have here the fundamental features of the contact-process as now employed, and Peregrine Phillips must be called its inventor in the same way as Dyar and Hemming are the inventors of the ammonia-soda process. The history of both inventions presents some common features. Made and patented in England, within a very few years of each other, by persons otherwise absolutely unknown, evidently neither trained chemists nor practical manufacturers in their respective lines, they remained almost unnoticed in the country of their birth; they were taken up in foreign countries, at first by men of science, afterwards by manufacturers, but only after having suffered many checks were they brought to full technical success, both abroad and in England, after an almost equally long interval, during which all attempts in that direction were judged hopeless.

Almost immediately after the publication of Phillips's patent, two German scientists repeated his experiments. Magnus (Pogg. Ann. 1832, xxiv. p. 610) found that 2 vols. sulphur dioxide mixed with 1 vol. oxygen (or more slowly with the corresponding quantity of air) is gradually condensed into sulphuric acid in the presence of water, but much more quickly in the presence of heated platinum, especially in the spongy state. Magnus also observed the formation of a little sulphuric acid on conducting the gaseous mixture through a darkly red-hot tube containing broken glass. At the same time Doebereiner (ib. p. 609) mentions that he had succeeded in condensing a mixture of 2 vols. sulphur dioxide and 1 vol. oxygen by the assistance of "hygroscopically moist" platinum black to fuming sulphuric acid. (The formation of what we now call "anhydride" had been also noticed by Phillips and Magnus.)

A. W. Hofmann, in his Report by the Jury on the Exhibition of 1862, p. 9, mentions a patent of Kuhlmann's, bearing upon the use of platinum as contact-substance for converting SO_2 into SO_3, dated Dec. 22, 1838. There is no English patent of this kind; probably it was a French patent.

In 1847 it became first known that a Belgian chemist, Schneider, had worked on "the manufacture of sulphuric acid and its concentration to 66° B. without lead chambers and platinum still by a contact-process." The first communication appeared in 'Dingler's Journal,' cvi. p. 395; further communications, all from French sources (Comptes Rendus, Moniteur universel, Bulletin de la Société d'Encouragement), in the same Journal, cvii. pp. 159 & 362, and cix. p. 354. The last is the most extended and contains both a description and somewhat detailed drawings of his apparatus. Schneider showed his process first to a number of Belgian gentlemen (among them Chandelon), afterwards to a committee appointed by the French Academy of Science, to which belonged Dumas, Pelouze, and Payen. Their report (by Payen) testifies that the process had been demonstrated by a model—that, in fact, sulphuric acid had been made without nitric acid or a nitrate, with a yield approaching that obtained in the actual manufacture (by the old system), and much greater than was attainable on the small scale without the action of porous bodies. Schneider employed as contact-substance pumice, prepared in a manner which he kept secret even before the examining committee, and which has never been divulged, so that we do not know whether his pumice was platinized (which is the most likely assumption) or prepared in any other way; his apparatus (which does not appear to have advanced beyond the stage of a working model) required, for the treatment of 800 kil. sulphur per diem, the considerable space of 500 cubic metres, with a contact-surface of 9500 square metres.

Schneider reports that already twelve years before, in March

1835, Clement-Desormes wrote to him as follows:—"I am convinced that in at most ten years it will be possible to make sulphuric acid on the large scale from its constituents without lead chambers, nitric acid or nitrates." But that was a wrong prediction (if ever made), and at all events was never realized "on the large scale" by Schneider, of whom the world has never heard anything since. We find no mention of *fuming* sulphuric acid in his publications.

Platinum in some shape or other has been alluded to by many inventors since Phillips. Already in 1846 (E.P. 11,425) J. T. Jullion mentions platinum sponge or "asbestos coated or covered with platinum" or other "catalytic or contact substances" heated to from 600° to 900° F. (316° to 482° C.); but he applies this only to the conversion of nitrogen oxides into "hyponitrous, nitrous, or nitric acid," and to that of hydrochloric acid vapours, by means of oxygen or air, while he makes sulphuric acid from water, sulphurous acid and chlorine without platinum. But a few years later we find platinized asbestos clearly indicated for the manufacture of sulphuric acid.

In 1852 Petrie (E. P. No. 590) mentions, besides siliceous matter and spongy platinum, also "filaments of asbestos coated with platinum." And in a specification, No. 188, of 1854 (not carried beyond provisional protection) W. H. Thornthwaite speaks of manufacturing sulphuric acid by carrying the vapours of sulphurous acid and the requisite quantity of common air, or passing the fumes from a burning mixture of sulphur and nitrate of potash, over a heated catalyzing agent, "by which a considerable saving of nitrate of potash is effected." As such "catalyzing agents" he specifies "*platinized asbestos* or other platinized substance not liable to change from the action of sulphuric acid, or the sesquioxide of chromium, of iron, or other sesquioxide."

In 1855 (Liebig's Jahresb. 1855, p. 308) Piria describes the preparation of *anhydrous* sulphuric acid by means of platinized pumice from SO_2 and air, or preferably oxygen. He had evidently been working entirely on a laboratory scale, but it is interesting to note that his special object was the preparation of sulphuric anhydride, not of ordinary acid, as most of the other inventors had in view.

Already Magnus, as we have seen, had united SO_2 and O by another "contact-substance" than platinum. In 1848 (B.P. No. 12,264), Laming applied for this purpose pumice-stone, prepared by boiling in concentrated sulphuric acid, immersed in water containing a little ammonia, dried and heated in a closed retort to near 600° F. (316° C.) with about one per cent. of peroxide of manganese, allowing it to cool out of contact with the atmosphere; he describes the product as a "catalytic porous body." The "sulphurous-gas is mixed with a due proportion of atmospheric air and a minute quantity of ammonia gas" (!), and is passed through vertical columns filled with the catalytic body and kept between 550° and 600° F. (288° to 316° C.); the sulphuric acid formed therein is washed out of the columns by water, a chimney maintaining a current throughout the whole conduit.

The next publication to be noticed is by Blondeau (Comp. Rend. 1849, xxix. p. 405). Starting from an observation made by Boussingault on the formation of sulphuric acid in some American rivers, near which the gases from burning sulphur ores came into contact with argillaceous sand and schist, Blondeau passed a mixture of sulphur dioxide, air, and steam through a red-hot porcelain tube filled with argillaceous sand, no doubt also containing ferric oxide. He obtained some sulphuric acid, but this was not followed up.

A few years later a very important further step was made for the introduction of other contact-substances than platinum.

Woehler and Mahla found in 1852 (Ann. Chem. Pharm. lxxxi. p. 255) that the *oxides of copper, iron, chromium*, best of all a mixture of chromium and copper oxide, brought to a low red-heat, caused the formation of thick fumes from a mixture of SO_2 and O. Platinum as sponge and sheet did not act at ordinary temperatures; but it acted far below red-heat, copper sponge only after superficial oxidation. Woehler's results gave an impetus to several trials at factories (for instance, at the Oker works), which, however, remained fruitless (Wagner's Jahresb. for 1859, p. 144), because the time required for the reaction was too considerable. I have made enquiries about the Oker trials in trustworthy quarters, which have shown, from official sources, that the experiments made there were performed in an iron tube, with a mixture of sulphurous acid vapours and air, and led to the condensation of acid of 5° B. in a lead tube fed with water. Evidently it was only a large scale laboratory experiment.

Woehler and Mahla already gave a correct interpretation of the catalytic action in this case, viz. the alternate reduction of

Fe_2O_3 and CuO to Fe_3O_4 and Cu_2O by SO_2, and their reoxidation by the oxygen; they also noticed that the formation of SO_3 took place without the presence of moisture; but as the attempts at utilizing the reaction on the large scale were made with a view of manufacturing ordinary sulphuric acid, there was probably no attempt made at including moisture, which is very prejudicial in this case, as we shall see.

Very soon after Woehler and Mahla's publication, Robb took out two English patents (No. 731 and 788, of 1853), in which he describes the manufacture of sulphuric acid by passing sulphurous acid from pyrites-kilns over peroxide of iron, resulting from the combustion of pyrites, heated to dull red-heat in a furnace or kiln kept hot by the pyrites-gases themselves, air being admitted at the bottom of the kiln. In his second patent he also mentions oxide of manganese and other substances, the whole to be coarsely powdered and made up into bricks, by means of clay or small coal &c., dried until they are hard. As we have seen above, Thornthwaite in 1854 also mentions the oxides of chromium and iron.

Trueman (E. P. 982, 1854) makes sulphuric acid from pyrites-kiln and other gases both by the help of platinum (either in the shape of wire or of pumice-stone or other porous substances impregnated with platinum chloride and ignited) and oxides of iron, copper, chromium, and manganese, broken into small lumps and kept at a red-heat.

Schmersahl and Bouck (E. P. 183, 1855) employ for the same purpose a mixture of sulphurous acid and air, passed through heated tubes, supplied with asbestos, or a mixture of copper and chrome oxides, platinum in wire or sheets, prepared pumice-stone, coke, animal or other charcoal, or other porous substances which afford an extensive surface. The gases are first passed through water previously to being combined with atmospheric air.

Silica is also mentioned as a catalyzer for the formation of SO_3; but the British patents quoted in support of this do not refer to this subject. Thus Petrie (B. P. 590, 1852; 2095, 1856) passes the gases from burning sulphur through towers filled with pebbles; but as these are to be fed with water, there is no question of "contact-action" as at present understood. W. Hunt (B. P. 1919, 1853) employs chambers or flues filled with pebbles or pumice or any other material capable of resisting the action of heat and acid, made nearly red hot by the heat of the burner-gases or by the spare heat from coke-ovens and the like. "By this means part of the sulphurous acid gas is made to take up oxygen from the air more readily than when the gases are comparatively cool." The sulphuric acid formed is carried forward with some sulphurous acid into a vitriol-chamber or into a condensing-tower fed with nitrosulphuric acid. Evidently Hunt did not contemplate a catalytic action in the proper sense (although this might occur to a slight extent), but merely the promotion of the union of SO_2 and O by the action of heat.

Plattner ('Die metallurgischen Röstprozesse,' Freiberg, 1856, pp. 334 *et seq.*) tried to carry out Hunt's proposal at the Muldenerhütte at Freiberg in such a manner that no fuel is required for keeping the silica serving as contact-substance in the hot state. He arranged two vertical flues within the roasting-kiln or heap, filled with lumps of quartz or siliceous slate, and made the roasting-gases pass through these flues. We may disregard the results obtained by analyzing a sample of gas drawn through caustic-potash solution, as this method yields altogether erroneous results, the sulphide in alkaline solution being quickly oxidized by the free oxygen present; but although, on the strength of these analyses, Plattner assumed that a large proportion of SO_2 had been oxidized to SO_3 (in one instance 30 : 1 !), and says that further experiments are to be made, no practical results have become known, and we may well imagine that the real formation of SO_3 was ultimately found to be too slight to be of any practical use.

Cl. Winkler, in his paper quoted below, mentions that Reich, in a pamphlet on the steps taken for dealing with the noxious vapours at the Freiberg works, speaks of experiments made on the same line as Plattner's, but that the effect was much too slow for practical use. Since Reich presumably used the same faulty analytical method as Plattner had done before him, we may take it that there is really nothing certain known about the contact action of silica, except that it is altogether insufficient for our present purpose.

Henry Deacon, the inventor of the celebrated chlorine process which bears his name, and which is based on the catalytic action of cupric sulphate or chloride, tried to apply this action (of course in this case that of the sulphate) to the manufacture of anhydrous or ordinary sulphuric acid (E. P. 753 & 1682, both of 1871).

Evidently he had no practical success in this direction, although his own energy and that of his gifted collaborator, Dr. Hurter, were sufficient to overcome any accidental difficulties. But it is interesting to note that he made two observations, important even to this day, viz.: that the *too sudden cooling* of gases after their treatment in the contact-apparatus should be avoided, and that the reaction goes on more favourably if an *excess of air or oxygen* is employed. His instruction as to the best temperature for the contact-process is certainly too vague to do much good, viz. "between that point at which sulphate of copper begins to be decomposed in a current of hot air and about that point at which tin melts." Another patent of his (No. 1908, of 1871) describes how the SO_3 formed by passing pyrites burner-gas, mixed with heated air, through a heated vessel containing burnt clay impregnated with a salt of copper is to be mixed with more air or oxygen and is to be made to act on $NaCl$ or KCl, in order to produce alkaline sulphates and free chlorine.

Up to the time to which we have now arrived in our historical survey, nearly all the attempts at uniting sulphur dioxide and oxygen by contact-processes had aimed at replacing the ordinary lead-chamber process, principally with a view of saving the great cost both of the plant and the nitre, which at that period was many times larger than it is at present, partly owing to the absence or imperfection of nitre-recovery apparatus, partly to the much higher price of nitrate of soda. Several of the inventors certainly speak of fuming sulphuric acid or of sulphuric anhydride, as we have seen, but none of them except Piria (who evidently thought only of laboratory work) places this in the foreground, for the simple reason that there was no market for large quantities of fuming sulphuric acid, and the requirements of the world, at that time, were easily met by the Bohemian works, which could have supplied considerably more of that article, if it had been called for, at such a low cost that competition by the contact-processes, in the imperfect state then known, would have been very difficult.

Just for this reason the various inventors took no special care in excluding moisture in their experiments, if they did not actually introduce water or steam on purpose; and precisely this circumstance caused the catalytic action to be very slow and imperfect, as moisture (at least when exceeding an extremely small quantity) seems to act as a "poison" for most of the reactions in question.

Nor was it sufficiently known up to that time (and much later) what great importance the complete removal of flue-dust and other impurities has for these processes, more particularly those employing platinum. This was first sufficiently proved by the patents of the Badische Fabrik. Last, not least, the development of chemical engineering was not sufficiently advanced to enable the manufacturer to transfer results gained in the laboratory to the large working scale as easily as this is the case at present. We surely need not wonder at the length of time which elapsed from the date of Phillips's patent to the actual introduction of the contact-process in our industry, if we consider that the working out of the ammonia-soda process to a real going affair did not require much less time.

The first of the above-named reasons for the slow development of the contact-processes, viz. the want of an extensive market for fuming sulphuric acid, was removed through the invention of the synthetical production of alizarine (which became a technical fact about 1872, having been first discovered in December 1868), and of other colouring-matters, equally requiring at intermediate stages of the manufacture the preparation of sulphonic acids, not obtainable except by the agency of fuming sulphuric acid. The demand for that article rapidly rose to such an extent that the Bohemian works founded upon the exploitation of "copperas-slate," all of which then belonged to the firm of J. D. Starck, could hardly supply it, and the naturally greatly enhanced price made this situation even more unbearable to the manufacturers of tar-colours. Many chemists at that period turned their attention towards the production of fuming sulphuric acid in other places and by other methods, either in the direction of carrying out the Bohemian process with some other and more suitable material than the Pilsen slates, or in that of applying one or more of the contact-processes invented from the time of Phillips onwards.

We have already mentioned (pp. 965 *et seq.*) the attempts in the former direction, which have all failed in the long run, and turn to the second class of processes. It is worthy of remark that the foundations had been laid long before by Phillips's patent for making sulphuric anhydride by the contact-process, and that only platinum and ferric oxide (which were used at a very early period), but no new catalyzers, have come into practical use up to the present time. To be sure, the recognition of the fact that for the platinum process *all* impurities, especially arsenic, must be removed, and that the heat of reaction is injurious and must be carried away, belongs to a later period and did not become known before the patents of the Badische Fabrik. But just that proposal which, at the turning-point at which we have now arrived, aroused the greatest attention, and professed both to explain the mishaps of former inventors and to usher in a period of more successful working, viz. the exclusion of an excess of oxygen as well as of inert gas, has proved to be a step in a wrong direction, which has caused the waste of very much time, energy, and money. Indirectly, however, it has been very useful in imparting fresh courage to those working in that field, and in first placing synthetically produced fuming sulphuric acid into the market.

The publication of Clemens Winkler's paper in Dingler's Journal, October 1875, vol. ccxviii. p. 128, is universally acknowledged to have been the opening of a new epoch in the history of the manufacture of fuming sulphuric acid, nay, although nobody dreamed of it at the time (as it has turned out), in that of sulphuric acid generally. That this was "in the air," that the practical introduction of contact-processes from one side or another was only a question of time, need not be said, and is best proved by the fact that almost on the same day that Winkler sent his manuscript to Dingler, W. S. Squire lodged an application for an English patent (No. 3278, Sept. 18, 1875), which, strange to say, embodies precisely the same idea (now known to be erroneous) concerning the best composition of the gases for the contact-process and the way of securing this composition by decomposing sulphuric acid itself by strong heat. This process was the common invention of W. S. Squire and Rudolph Messel. The two authors a little later (April 20, 1876) read a paper concerning their process before the Chemical Society, but it does not appear in their Transactions. I am, however, enabled, by the kindness of Dr. Messel, who has sent me a manuscript copy of that paper, to quote a few points of historical interest from it. The inventors were, like Winkler, induced to try the catalytic process by the sudden rise in the price of fuming oil of vitriol, and they tested the action of pumice impregnated with a solution of platinum chloride and ammonium chloride, heated to dull redness, on a mixture of the vapours of burning sulphur and air, or of SO produced from copper and sulphuric acid, with just enough air to oxidize the SO_2.

Dense clouds of SO_3 were at once observed, but could not be properly condensed. This was, however, possible when passing a mixture of pure SO_2 and oxygen in the requisite proportions over spongy platinum. "The whole, or very nearly the whole," of the SO_2 was oxidized, and in the absence of foreign gases the condensation of liquid SO_3 was "extremely perfect." The next step was to prepare the mixture of SO_2 and O on a commercial scale; and the inventors, like Winkler, bethought themselves of Deville's celebrated process of preparing oxygen by subjecting sulphuric acid to a high temperature. They boiled strong sulphuric acid in a small platinum still, passed the vapours through a platinum tube kept at nearly white-heat, cooled and dried the vapours issuing from that tube and passed them through a second tube containing platinized pumice kept at a dull red-heat. Thus they obtained nearly 70 parts of SO_3 from 100 parts of white sulphuric acid.

They further tried Woehler and Mahla's mixture of the oxides of chromium and copper, made into pills with asbestos and heated to redness; but they preferred to employ spongy platinum in an apparatus erected at Silvertown, capable of producing some tons of anhydrous SO_3 per week, which was nearly ready for starting at that time (April, 1876). They ultimately note that the loss of activity of the catalytic agent is due to the accumulation of foreign matter, such as flue-dust, which would not exist in their process of preparing the mixture of SO_2 and O from strong sulphuric acid. (Arsenic, however, is not mentioned here, and the importance of excluding even the smallest traces of volatile arsenic compounds as a "contact poison" was evidently quite unknown at that time.)

Winkler's paper of 1875 deals firstly with the imperfections of the Bohemian process and the attempts at making it generally accessible by reconverting the ferric oxide into sulphate by means of ordinary sulphuric acid (comp. p. 965), which do not remove the principal objections to that process. He then turns to the attempts at the synthesis of SO_3 from SO_2 and O by contact-substances, among which platinum in a finely divided state is the most efficacious. The platinum should be spread over as great a surface as possible, and so-called platinized asbestos has been especially recommended for this purpose. [As we see, Winkler does not claim to have first proposed platinized asbestos, which had long before been used by Jullion, Petrie, and Thornthwaite, p. 977.] Pumice or porous porcelain are much less efficacious [comp. below, Winkler's later experience, contrary to the above]. The action of platinized asbestos is, however, very different according to the state of dilution of the gases. In a mixture of pure SO_2 and pure O, 73·3 per cent. of the SO_2 was converted into SO_3, in a mixture of pure SO_2 and air only 47·4 per cent., and in a gas produced by burning sulphur in air, and containing 4 or 5 per cent. SO_2, only 11·5 per cent. Winkler concluded from this that the action of contact-substances is diminished by the presence of inert gases, and, as a matter of course, an excess of sulphur dioxide or oxygen remains indifferent, and therefore acts as a diluent. Hence the two gases should be employed in the exact stoechiometrical proportion, in which case only can we expect a quantitative conversion of SO_2 into SO_3. [The above is in contradiction to the law of the action of masses, which was almost unknown to chemists at that time, and it has been recognized as erroneous by Winkler himself and everybody else: comp. Deacon, p. 981.]

In order to obtain such a stoechiometrical mixture of pure SO_2 and O, without diluent gases, in the exact proportions, Winkler proposes to make use of the well-known fact that ordinary concentrated sulphuric acid is by strong heating decomposed into sulphur dioxide, oxygen, and aqueous vapour; the latter is completely condensed and removed by absorption in strong sulphuric acid, and the remaining dry mixture of SO_2 and O exposed to the action of platinized asbestos at a low red-heat ("gelindes Rothglühen"). He describes a laboratory experiment made on those lines, in which 93 per cent. of the strong sulphuric acid was decomposed and 78·4 per cent. of the decomposed acid (or 73·7 per cent. of the total acid employed) was converted into SO_3. On this he founds proposals for carrying out the process on a large scale which we need not repeat, as that process soon after was recognized as too expensive, perhaps first of all (as we now know) by the inventor himself.

(We must notice here that the yield of SO_3 found by Winkler, although it seemed encouraging enough at a time when only the manufacture of fuming acid was thought of, and when that acid cost many times as much as ordinary sulphuric acid, would be called at the present time much too low even to pay for fuming acid.

Of course longer practice would probably have led to a somewhat better yield, but we now know from theoretical considerations that the maximum yield obtainable from SO_2 requires *more* than the stoechiometrical proportion of oxygen to be employed.)

Winkler also mentions the possibility of the contact action of platinum being destroyed in course of time; but this, he says, can be caused only by flue-dust and other extraneous impurities, which are excluded in his process of obtaining the gaseous mixture by decomposition of sulphuric acid.

A little later (Dingl. Journ. 1877, ccxxiii. p. 409) Winkler still defended his process against the objection of Debray, according to whom the decomposition of sulphuric acid requires too high a temperature and causes a rapid destruction of the apparatus, whether made of metal or earthenware; but very soon after, as we shall see later on from his own statement, he must have convinced himself that Debray's objections were only too well founded.

The publication of Winkler's paper acted upon the industrial chemical world like a sorcerer's wand upon pent-up spirits. The fatal spell hitherto resting upon the synthesis of sulphur trioxide by catalytic action seemed to be broken; the relieving word seemed to have been found, which explained all the miscarriages of former inventors, viz. that pure sulphur dioxide and pure oxygen should be present in the theoretical proportion, without an excess of either or any inert gases; and although the method of securing this, the splitting up of sulphuric acid, was evidently an expensive one and could of course never be dreamt of for the manufacture of ordinary sulphuric acid itself, this did not debar the expectation that the new process would break the monopoly of the Bohemian works for that expensive article, *fuming* sulphuric acid.

In Great Britain certainly Squire's patent barred the way except for the firm to which the patent belonged; but in Germany the road was free, as the patent law for the German Empire was only introduced in the following year, and Winkler had not taken out patents for the single German states. Any number of chemists in that country, where the sudden expansion of the coal-tar colour industry made the want most urgently felt, threw themselves upon this promising path. It is curious to notice that precisely the want of patent protection for Winkler's process, much as it stimulated the efforts of other chemists in one way, had a harmful effect in another direction. Just because no patent stood in the way, a number of factories sprung up in Germany for the purpose of carrying out Winkler's process, and all efforts were directed towards overcoming the technical difficulties of decomposing sulphuric acid into SO_2, O, and H_2O, which are caused by the very high temperature required for this reaction, and the immense corrosive action of the substances in question on the material of the apparatus. It took much time, labour, and capital before it was recognized, both that this part of the process was much too difficult and expensive for practical purposes, and that it was worse than unnecessary even to aim at producing an exact mixture of 2 vols. SO_2 and 1 vol. O_2. If other chemists had been compelled, by the existence of a patent for Winkler's process of 1875, to turn their attention in another direction, their labours would have been much sooner rewarded with success. The loss of time and trouble in this matter is very strongly expressed by Ostwald (Zsch. für Elektrochemie, 1902, viii. p. 154), who says that every chemist acquainted with Guldberg-Waage's law might, a quarter of a century ago, have read the fallacy of Winkler's reasoning from the equation of the reaction. But it is only just to Winkler to point out that in 1875 and very much later hardly any chemist, scientific or practical, did pay attention to Guldberg-Waage's law in his reasoning. Winkler's paper notoriously at once roused quite as much attention among purely scientific as among practical chemists. Probably every professor of chemistry has mentioned it in his lectures from that time to the present, and most of them have demonstrated his experiment in their lectures. Why was Winkler's reasoning never protested against, as contrary to the above law, until Knietsch did so in 1901? Nobody can blame Winkler for his mistake in neglecting that law in 1875, a mistake which practically every professor of chemistry has committed who has quoted his work without criticism, as they all did until the most recent times. Winkler indeed was quite in the right when trying to exclude nitrogen as an injurious diluent, and he erred only in considering any oxygen present over and above the stoechiometrical proportions as an equally injurious diluent.

One of the first who recognized the fact that the preparation of a mixture of exactly 2 vols. SO_2 and 1 vol. O_2, without any other gases, was unnecessary, and, as we now know, not even suitable for the purpose in question, was Winkler himself, as we shall see later on; but this remained a profound secret for many years, up to 1900, and during the first few years after 1875 the original Winkler process, based on the decomposition of sulphuric acid into SO_2, O, and H_2O at a very high temperature*, ruled the exertions of most or all German chemists. A number of factories founded upon that process soon sprang up, as there was an enormous margin between the cost price of fuming O.V. and its selling price at that time (*2s. 6d.* per kilogram of SO_3 contained in fuming O.V.). The monopoly of the Bohemian works was thus broken.

I cannot ascertain when the first fuming acid made by synthesis at the Silvertown works came into the market. In Germany this was undoubtedly the acid made by Dr. Adolph Clemm in 1877, as mentioned p. 969, by the bisulphate method. Soon after followed Dr. Emil Jacob in Kreuznach, who apparently worked first by Winkler's method, but later on with gases from burning brimstone.

An authentic report respecting the work carried on in secrecy at Freiberg, from 1877 onwards, will be found later on.

From communications by Dr. Emil Jacob, and original documents submitted by him, it appears that he supplied large quantities of 43 per cent. fuming acid to the Höchst works in 1879. In 1880 the yield of such acid, starting with strong sulphuric acid (66° B.), was 61·9 per cent., in 1882 already 70·4 per cent. The following is a cost sheet for four months, commencing Jan. 1, 1882:—

	Marks.
258,408 kil. acid 66° B.	22,988
32 truckloads coal	4,000
Wages	3,600
Repairs and replacing apparatus	2,800
Amortization 10 per cent. on 24,000 Marks (cost of plant)	800
Cost of 181,990 kil. fuming acid (43 per cent. SO_3) (without packages)	34,188
Selling price of same	67,340
Besides 43 tons weak acid 27° B.	

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* In Germany the expression "Winkler's process" is frequently, but altogether erroneously, applied to the production of sulphuric anhydride by platinum catalysis generally. Evidently that expression should be confined to that modification of the catalytic process which is mentioned in the text, as published by Winkler in 1875, and simultaneously and independently invented by Squire and Messel.

On August 17, 1882, Dr. Jacob sold his process, which was at that time the same as the Winkler process of 1875, to Messrs. Meister, Lucius, & Brüning, who forthwith introduced it at their Höchst works. But in 1886 he started working with pyrites-gases, and in 1887 with brimstone-gases which answered very well.

About that time the Ludwigshafen factory commenced work, but the precise time does not appear clearly from the statements of Knietsch (Berichte, 1901, p. 1477).

At nearly the same time the Thann Chemical Works, in Alsace, proceeded on other lines. The following communications as to their hitherto entirely unknown doings are due to the kindness of M. Meunier-Dollfus, the surviving partner. In September 1878 the above firm made a contract with the firm of Chapman, Messel, & Co., of London and Silvertown, for the purchase of the process patented by W. Squire in 1875 and following years, founded (like Winkler's process) on the decomposition of strong sulphuric acid by heat. While the preliminary researches were going on for adapting and installing that process at Thann, Mr. Squire, who had in the meantime severed his connection with the London firm, offered to the senior partner of the Thann firm, M. Scheurer-Kestner, a new process invented by him, as being greatly superior to the process then at work at Silvertown. It was resolved, in accordance with the London firm, to study the new process and to introduce it at the Thann works as soon as possible. These studies commenced in April 1879, and after gradually overcoming manifold difficulties, they led to a very satisfactory solution of the problem. Sicilian sulphur was burnt as usual and the gases were treated with water in a column apparatus under a pressure of four atmospheres. The SO_2 was expelled by steam from the solution thus obtained, then mixed with the theoretical quantity of air and passed over heated platinum asbestos. The SO_3 formed was absorbed in towers by concentrated sulphuric acid, and fuming acid of 40 per cent. SO_3 was thus obtained. The exit-gases, still containing SO_2, were passed back into the process. The daily make was 30 cwt. SO_3, and the yield 90 per cent. of the theoretical. At the beginning of 1881 this process was in regular working order at Thann, and it was subsequently also introduced at Ludwigshafen.

Except what I am enabled to quote from M. Meunier's communication, nothing else is known about the work done at the

Silvertown works since 1876, which have certainly been producers of fuming sulphuric acid ever since that time.

The firm of J. D. Starck, when it saw its monopoly broken through in the manner described, combined with the works at Mannheim, Kreuznach, Höchst, and Thann for keeping up the prices of fuming O.V., and this agreement lasted until the Badische Fabrik came into the market with such large quantities that the "combine" gradually dissolved.

The further history of the manufacture of sulphuric anhydride by the contact-process up to 1900 was enveloped in great mystery, but sparely enlightened by the patents taken out in the meantime, and by a very few glimpses from the practical experiments carried on at various German factories. These experiments were surrounded with all the more secrecy, as there seemed to be so little ground upon which patents could be based after the great number of previous publications on the subject of contact-processes. This period lasted till the publication of the first patents of the Badische Fabrik, which usher in a new epoch. What has been done in the meantime is now, to a great extent, cleared up by the publications of Winkler (in 1900), of Knietsch (1901), and by the special communications which I am enabled to give later on. First, however, we shall follow up what can be gleaned from the patents and a few other notes during the period following the publication of Winkler's first paper.

As previously stated, the first years of that period were mainly spent in attempts to carry out Winkler's process on the large scale. The abandonment of this process was caused by the difficulties mentioned by Debray (p. 986), especially during the decomposition of the sulphuric acid. The greatest difficulty in Winkler's process for manufacturing fuming oil of vitriol or anhydride, and in all other processes started in consequence of the impetus given by him, is indeed the material of the vessels to be employed. Wallace, in his patent of May 30, 1876 proposed to employ glazed plumbago retorts. Some factories seem to have employed platinum vessels, which are, however, strongly acted upon, as was shown by Scheurer-Kestner (see above). The extent of this action partly depends upon the amount of arsenic and nitrous acid contained in the sulphuric acid (comp. Wagner's 'Jahresbericht,' 1877, p. 238), partly also upon the special construction of the apparatus. According to communications received direct by me from Dr. Majert, the apparatus employed by him at the Schlebusch works, near Cologne, was arranged as follows (comp. also his French patent No. 122,130, of Jan. 16, 1878) :—The decomposition of sulphuric acid into SO_2, O, and H_2O was effected in upright retorts made of a mixture of 3 parts burnt fire-clay broken to the size of a pea, and 1 part best Belgian fire-clay, and glazed with a mass which at the highest temperature of the process becomes pasty but not liquid, so that any cracks occurring in the retort become filled with the glaze. The retorts were perpendicular, entirely surrounded by the fire, and closed at top and bottom by hydraulic joints. The top joint served for introducing the pipe conveying the acid to be decomposed, the bottom joint for making the sides of the retort tight in the fixed bottom, which is perforated by the pipe which carries off the gases. Both the "hydraulic" joints, which were entirely surrounded by the fire, were luted with melted glass. Within the first retort there was a cylinder, into which the vitriol flowed from a small platinum tube, so as not to touch the sides of the retort at all. It was thus evaporated within the inner cylinder, and partly decomposed there, partly in the annular space between the cylinder and the retort, and completely in the second retort. The vapour and gases were conveyed from the first to the second retort by a twice-bent tube, which passed through the bottoms of both retorts, and whose horizontal part was surrounded by the flame of the fireplace. The gases passed away from the top of the second retort into a condenser for liquefying most of the water, then into a drying-tower, and at last into the apparatus for uniting SO_2 and O, consisting of cast-iron retorts filled with wire-gauze shelves, upon which the platinized asbestos was spread. (This factory has not been at work for a long time.)

Angerstein (G. P. 26,959, Sept. 14, 1883) describes a special apparatus for decomposing the sulphuric acid, which is supplied from below, is evaporated in a shallow platinum dish, and decomposed in fire-clay pipes filled with broken fire-bricks, and heated outside to a very high temperature by the combustion of gaseous fuel under pressure.

According to a German patent of Squire's (No. 4285, March 3, 1878), strong vitriol is introduced into a red-hot tower packed with hollow bricks and previously filled with dry steam. The vitriol is in the form of a mist, produced by a compressed gaseous mixture of sulphurous acid and oxygen. The products of decomposition are conveyed in a horizontal closed channel through a lead pan filled with dilute sulphuric acid, where the water is condensed by cooling, whilst the heat of the gases concentrates the sulphuric acid contained in the pan and frees it from sulphurous acid. A further condensation takes place in cooling-pipes; and ultimately the gases are dried in a coke-tower by means of strong sulphuric acid, which is again concentrated and freed from SO_2 in the lead pan just mentioned. The dry mixture of SO_2 and O is combined into SO_3 in a specially heated apparatus made of cast iron outside and brickwork inside, fitted with a pyrometer, where it is brought into contact with platinized asbestos, being forced to travel a circuitous path between courses of bricks. The vapour of anhydride is absorbed by strongest vitriol in a cast-iron tower, fitted with dishes of a peculiar shape, placed one over another. (The specification gives further details and diagrams of the apparatus.)

After a few years the decomposition of sulphuric acid by heat, for the purpose of obtaining a suitable mixture of SO_2 and O, was given up everywhere, owing to the great expense of the process and the extreme wear and tear of the apparatus. But the belief, that the gases should be combined in stoechiometrical proportions and as little as possible diluted with inert gases, was still prevalent and led to a number of attempts at producing the same effect in a cheaper and more practicable way than that indicated by Winkler and by Squire and Messel in 1875. Those proposals which have been made public are the following:—

J. Neale (English patent No. 1103 of March 14th, 1876) heats anhydrous sulphates or bisulphates of iron, zinc, aluminium, or sodium in earthenware retorts or muffles, and conducts the mixture of sulphurous acid and oxygen formed by their decomposition over heated spongy platinum, or the oxides of chromium, iron, or copper, or any other substance which may cause the mixture to combine into sulphuric anhydride. The latter is then condensed by itself or utilized for fuming oil of vitriol by receiving it into ordinary strong sulphuric acid.

Scheurer-Kestner (Compt. Rend. xcix. p. 876) asserts that on heating a mixture of 2 parts of anhydrous calcium or magnesium sulphate with 1 part of ferric oxide to a bright red-heat, all the sulphuric anhydride is driven off, at first as such, afterwards decomposed into SO_2 and O. By mixing 175 parts of gypsum with 100 of fluorspar and ferric oxide, the decomposition takes place at a lower temperature (that of the Bunsen burner) and the SO_3 is then not dissociated into SO_2 and O.

To avoid the dilution of sulphur dioxide with excess of air and of nitrogen, unavoidable when burning sulphur or pyrites, and which at that time was still considered very injurious for contact-action, Schroeder and Haenisch proposed to employ the pure SO_2 obtained by their process in a somewhat costly manner (p. 381). The application of this to the manufacture of SO_3 forms the subject of their E. P. 9188, 1887.

A mixture of pure sulphur dioxide and air in a certain fixed proportion is passed at a low red-heat, and under pressure, over platinized asbestos, whereby a large surface and a lengthened duration of contact are ensured to the gases. The pressure also promotes chemical reaction by bringing nearer together the active gas-molecules. A gas-mixture consisting of 25 per cent. SO_2 and 75 per cent. air is most suitable for the process; the mixing of the gases simultaneously with their compression is effected by a double cylinder compressor, the two cylinders of which have a cross-sectional area in the proportion of 1 : 3, so that one cylinder pumps three times as much air as the other pumps sulphurous anhydride. The compressed gases meet in the conducting-tube and pass into an air-chamber, and thence into the combining-apparatus. This consists of two horizontal wrought-iron tubes, set in a furnace, of somewhat narrow diameter and strong walls, sufficient to stand a pressure of several atmospheres at a dark red-heat; they are filled with platinized asbestos prepared in a special manner. The pressure (usually 2 to 3 atmospheres) is regulated by a valve at the common exit-tube. Here most of the SO_2 is converted into SO_3; and lest this should deposit in a solid form in the tubes or in the valve, the parts projecting from the furnace are surrounded by a leaden steam-coil. If, in spite of this, there should be some obstruction by the crystallization of SO_3, the pressure in the air-chamber will raise a valve, weighted about 1 atmosphere, above the exit-valve. From the latter the remaining gases pass through condensing-jars, where the SO_3 deposits in the solid form or is retained by strong sulphuric acid. The SO_2 still present is separated from the nitrogen by water and used over again. This process was carried out in one or two places and worked quite well, until the development of the processes dealing with pyrites-kiln gases made it unprofitable (comp. Dr. Schroeder's communication to myself later on).

The task was also approved from the other side, viz. excluding the nitrogen of atmospheric air. This was first proposed by Messel (E. P. No. 186, Jan. 15, 1878). He prescribes burning sulphur by means of oxygen, obtained by the electrolysis of acidulated water with the help of dynamo-electrical machines. The sulphur dioxide formed, mixed with the excess of oxygen required for forming SO_3, is conveyed into a gas-holder, from which the gases are carried at a high temperature over spongy platinum, platinized asbestos, oxide of chromium, iron, or copper. The anhydride formed is condensed by itself or absorbed in sulphuric acid. By employing two gas-holders the process is made continuous. The electrolytical hydrogen formed at the same time is employed for heating, or it is carburetted and employed for lighting. This process must have been too expensive, owing to the cost of electrolytically-made oxygen. When that gas became a cheap commodity through the development of Brin's processes, I myself (Ellice-Clark's patent, No. 3166, 1888) proposed utilizing such oxygen in a similar manner, in such a way that no external heat should be required, and there should be no waste gases of any sort. I abstain from giving a detailed description or drawing of the apparatus proposed by me, as it is now certain that the admixture of nitrogen does not, as formerly assumed, prevent a complete oxidation of SO_2, provided the contact-substance is sufficiently active; this circumstance deprives the pure oxygen of its advantages in comparison with atmospheric air.

The task of manufacturing sulphuric anhydride in a sufficiently cheap manner could not be regarded as solved until it had been proved that gases from *sulphur-burners*, or, still better, from *pyrites- or blende-burners*, could be employed for this purpose.

Clemens Winkler himself speedily recognized this when trying to carry out his process on the large scale: he had already, about 1877, suggested the employment of pyrites-burner gases, as mentioned by him in 1900 (Zsch. angew. Ch. 1900, p. 738; comp. a previous notice by myself, *ibid.* p. 80); but this suggestion, as well as its practical pursuit and the partial success ultimately obtained in this direction, remained an absolute secret of the factories at Freiberg and Stolberg. We shall refer to this subject more in detail later on.

In his paper of 1900, Winkler mentions the great difficulties which had to be overcome in purifying the gases from flue-dust, in order to preserve the action of the catalytic substance. These difficulties were, according to his statement, avoided by Jacob, of Kreuznach, through the employment of gases from burning brimstone (comp. p. 988).

A French patent, not mentioned anywhere in the published literature, was taken out by Lange and Göpner (No. 123,906, on April 16, 1878), for treating ordinary pyrites-kiln gas (of whose purification nothing is said) by red-hot pyrites-cinders, or platinum sponge, or analogous substances in tubes made of graphite, cast-iron, and the like, in order to produce sulphuric anhydride or fuming O.V. No details are given respecting the apparatus or method, and such a general claim would of course have been quite untenable. No English or German patent exists for this "invention."

In 1878 Messel took out provisional protection (No. 1201) for making monohydrated sulphuric acid by means of SO_3 produced by catalytic action from the gases of burning sulphur. This patent was not completed.

The first mention of employing ordinary pyrites-burner gases which I can find in the printed literature since 1875 is the following, much later than (as we now know) the actual work secretly done in that line at several factories.

Rath (G. P. 22,118 of 1883) passes pyrites-burner gases, to free them from most of the water, through a cooling-apparatus, consisting of a large number of perpendicular lead pipes placed in cold water, at a velocity not exceeding 5 inches per second. Air may be admitted to them by means of a valve. From the cooler the gases pass through a coke-tower fed with acid of 140° Tw. In order to be thoroughly dried here, the velocity of the gaseous current should not exceed 2½ inches. From here the gases are aspirated by a pump and forced through a number of iron retorts, lined with clay, which contain the contact-substance, and are heated to a temperature between dark and bright red-heat. The number and size of these retorts must be chosen in such a manner that the velocity of the gases does not exceed 2½ inches. The sulphuric anhydride formed here is either condensed in the liquid form in tin-plate vessels standing in a place heated to 25° to 30°, or else it is passed into cast-iron vessels charged with sulphuric hydrate and kept at 25°. Special precautions are required for gases containing carbon monoxide or hydrocarbons. According to Knietsch (Ber. 1901, p. 4078) nothing is known as to the practical success of the above process.

The later history of this part of our subject is contained in the various communications given below from the firms now working on the large scale.

Theory of the Contact-Processes for the Manufacture of Sulphuric Anhydride.

We have now passed in review the former stages through which the contact-processes in our field have gone. Before proceeding to describe the present state of this industry, we shall interpose a discussion respecting the theoretical side of this problem.

We have before (p. 974) briefly referred to the very uncertain views of Berzelius on contact or catalytic action, and to the ideas concerning a particular class of such action which for a long time were universally accepted, which, however, do not embrace the whole field of catalytic actions, but mainly those where solid porous bodies come into question, which would certainly apply to our present case. But even for this the explanation, according to which those reactions are caused by the condensation of gases within the pores and the greater mutual attraction of their molecules under this condition, is not at present held to be correct or at least not sufficient.

Liebig attempted to explain catalysis in this way: that a substance (the catalyzer) whose molecules possess a "chemical motion" may impart that motion to another substance present and may thus cause a chemical reaction which that substance would not have undergone without the presence of the catalyzer. This "explanation" is certainly quite hypothetical and incapable of direct proof; it did not in reality make the matter clearer, nor could it assist in discovering new facts, which is the real test of a "working hypothesis"; but Ostwald is hardly just in saying that Liebig thereby retarded the investigation of the problem of catalysis by half a century. It is a fact that Liebig's explanation was never anything like generally acknowledged among chemists as a true solution of the problem, and it could not therefore retard the progress of science.

Liebig's explanation of catalysis, so far as it went, applied more to the phenomena of catalysis among liquids than to those which interest us in this place, and we will not detain ourselves with it.

A somewhat clearer explanation of catalytic actions has been given by Bunsen, in his 'Gasometrische Methoden,' 1st ed. p. 267. Chemical combinations are not dependent entirely upon the mutual attraction of the substances entering into combination, but also upon the attraction of other substances which are present, but do not take part in the combination; in other words, these combinations are the resultant of the attracting forces exerted by *all* the molecules present in the sphere of the chemical action, whether these molecules take part in the combination or not. For instance, the elements composing hydrogen peroxide are capable of uniting in the attraction sphere of water molecules, but not in that of metallic oxides or of platinum. Thus there is some analogy of catalytic action with that of masses, as has been pointed out elsewhere.

Bunsen's theory probably contains elements of truth, but is hardly of a kind to help us understand the special cases under consideration. We may pass over several other physical or mechanical theories of catalysis (comp. Fehling's Handwörterb. der Chem. iii. p. 945) and turn to the chemical theory of catalysis.

Ostwald (' Grundriss der allgemeinen Chemie,' 3rd edit. p. 515) explains a catalyzer as a substance which, without appearing among the final products of a reaction, alters its velocity. He has (comp. p. 773) applied this even to the manufacture of sulphuric acid by the vitriol-chamber process. He says: "sulphur dioxide is oxidized by air and water alone to sulphuric acid, but very slowly; the presence of nitrogen oxides merely hastens this process." Nobody will or can deny this, but Ostwald, as we have seen (p. 774), seems to go too far in neglecting the importance of the intermediate reactions as if they were unessential and accidental. Quite the contrary, the investigation of these intermediate reactions seems to be a step towards a *real* explanation of the otherwise enigmatic "change of velocity" of the reaction in question.

Evidently even in the case of platinum as a catalyzer, one of the simplest cases of catalytic action, the formula of Ostwald is *too* simple and cuts the knot instead of untying it.

This seems to be confirmed by the behaviour of another catalytic substance which comes into play in this our present subject, viz. ferric oxide. This agent may be taken as playing an intermediate part between the action of platinum and that of the nitrogen oxides. It is a solid substance of porous nature, not known to be particularly active in condensing gases by its physical character (let alone liquids!), and it acts only at a high temperature on a mixture of $SO_2 + O$, similarly to platinum. But, on the other hand, it does form a compound with the product of the reaction; this compound, $Fe_2(SO_4)_3$, exists as such at comparatively high temperatures, viz. just below a dark red-heat, and decomposes again into Fe_2O_3 and $3\,SO_3$ at a temperature not far removed from that which has been observed as the optimum for the "catalytic" action of ferric oxide. Here the explanation of the catalytic action seems to be this: by the interaction of Fe_2O_3, O, and SO_2, many molecules of $Fe_2(SO_4)_3$ are formed, but as the temperature at which this compound is split up into Fe_2O_3 and $3\,SO_3$ is very nearly the same as that at which it has been formed, that splitting up actually takes place, SO_3 is removed in the state of vapour, and Fe_2O_3 is again at disposal for combining with SO_2 and O. This explanation deals with reactions and substances actually and easily observed, and we have a right to assume that it certainly does come into play, a state of equilibrium being established for each temperature, in which a certain number of molecules of $Fe_2(SO_4)_3$ are formed and others are split up into Fe_2O_3 and $3\,SO_3$. At the same time another set of reactions is possible and indeed quite as probable to take place, although the conditions of equilibrium may here lead to a different optimum of temperature. These are the reactions: (1) $3\,Fe_2O_3 + SO_2 = 2\,Fe_3O_4 + SO_3$, and (2) $2\,Fe_3O_4 + O = 3\,Fe_2O_3$.

Precisely in the same way the catalytic functions of chromium oxide, of cupric oxide, sulphate, or dioxide, and all other substances can be explained which are subject to easy changes of valency and therefore form two or more sets of compounds with oxygen, chlorine, or acid radicles.

A very interesting paper by Manchot and Wilhelms (Berl. Ber. 1901, p. 2479) shows that the catalytic action of the salts of iron may be due to the intermediate formation of a peroxide, FeO_2; but as their work extended only to reactions in the wet way, we cannot take it into account for our present purpose.

Most or all chemists have recognized the just mentioned intermediate reactions (comp., *e. g.*, Woehler and Mahla, p. 978), but the majority of chemists preferred to consider the action of platinum, which is so manifestly aided by its division over great surfaces, as different from the former class of processes. Platinum was generally regarded as having no affinity for oxygen at the temperature of the reaction, and as acting merely by condensing gaseous bodies in its pores. But there were always chemists who believed in the transitory formation of platinum oxides, and Engler and Woehler (Zsch. anorg. Ch. xxix. p. 1) have definitely proved that a platinum peroxide exists in platinum black, which acts as an oxygen carrier, so that they class all platinum catalysis as "pseudo-catalytic"—that is, as brought about by intermediate reactions which go on much more quickly than the direct action. We may take it as probable that ultimately most, if not all, "catalytic" processes will be recognized as "pseudo-catalytic" in that sense.

Already before these publications, Haber and Grinberg (Zsch. anorg. Ch. xviii. p. 39; Zsch. f. physik. Ch. xxxiv. p. 515) and Bredig (*ibid.* xxxi. pp. 294, 346, and 'Anorganische Fermente,' 1901, p. 942, with his cooperators Müller von Berneck, Ikeda, and Ernst) had pointed out that in platinum catalysis the first phase is the formation of a platinum oxide (otherwise shown to probably exist by the experiments of Mond, Ramsay, and Shields, Zsch. physik. Ch. xxv. p. 685), which is reduced in the second phase, *e. g.* by H_2O_2, with evolution of oxygen.

Brode (Zsch. f. physik. Chemie, xxxvii. p. 257) has, in the case of molybdenum and tungsten compounds as oxygen carriers, shown the quantitative kinetic working of the intermediate reactions in catalysis.

We now pass on to the special processes going on when sulphur dioxide and oxygen are made to combine by contact-action. Here we enter upon the experimental field. We have quoted (p. 985) Winkler's trials of 1875, in which he succeeded in recombining 78 per cent. of the mixture of SO_2 and O, obtained by decomposing H_2SO_4 by strong heat. No higher figures of yield are recorded anywhere else for Winkler's process in literature; although it was undoubtedly repeated hundreds of times on the small and also on the large scale, nothing was published about it till we come to the work of Knietsch. We do not therefore know what are the best results obtainable with that process, but even from theoretical considerations we may conclude that it could never lead up closely to a *complete* conversion of SO_2 into SO_3. This is, for instance, pointed out by Sackur (Zsch. f. Elektrochemie, viii. p. 47). To expect that 1 mol. SO_2 could be converted into SO_3 by a single atom of O is contrary to the law of the action of masses. Since the reaction $2\,SO_2+O_2 \rightleftarrows 2\,SO_3$ is reversible, that law leads to the equation $\frac{(SO_2)^2 \times (O_2)}{(SO_3)^2}=k$; hence $\frac{SO_3}{SO_2}=\sqrt{\frac{O_2}{k}}$, which means that the yield of SO_3 is the larger, the greater the concentration of the oxygen. The same author maintains that in theory dilution with nitrogen must influence the yield unfavourably; but in practice this does not matter, as the gases are not diluted with pure nitrogen, but with air, and thus the concentration of oxygen is increased at the same time, which alone is decisive for the yield.

E. J. Russell and Norman Smith (Journ. Chem. Soc. 1900, lxxvii. p. 340) have made some interesting experiments on the combination of sulphur dioxide and oxygen. They found that even at the ordinary temperature certain metallic oxides (MnO_2, PbO_2, CrO_2, Fe_2O_3, Cr_2O_3, and the hydroxides of these metals) cause the two gases to combine to a certain degree, in proportion to the extent of surface presented by the oxide. The amount of combination also depends on the state of the surface; it is least with freshly precipitated oxides which are not yet dried, and increases if the oxide has been moderately heated or kept for a long time so as to become dry. There is in every case simultaneous combination of the oxide with the SO_2. The most striking instance of this surface-action is afforded by MnO_2, some 20 per cent. of the SO_2 being converted into SO_3. If the materials are carefully dried by phosphorus pentoxide, no combination takes place even after several days. In this case the combination of MnO_2 and SO_2 is prevented, as is also the surface-action of the oxide which brings about the union of SO_2 and O.

All these experiments were made at ordinary temperatures, but platinum (in the shape of platinized pumice) was tried at a temperature of 400° to 450°. When SO_2 and O are passed over it, combination diminishes, as the materials are more completely dried by phosphorus pentoxide, and can be made very small; probably it would be *nil* if all moisture could be absolutely excluded, which is very difficult even after treating the substances for weeks with P_2O_5. As soon as steam was introduced, a combination took place which was driven to the extent of a contraction of 56 c.c. in a mixture of 250 c.c. oxygen and 65 c.c. sulphur dioxide, after an action of 24 hours.

[These experiments harmonize with those of Dixon and Baker, showing that neither carbon monoxide nor hydrogen combine with oxygen when all water is absolutely excluded. But evidently the beneficial influence of water in this case very soon reaches its maximum, when only traces of H_2O are present, and very rapidly declines, in order to produce later on the opposite effects, for there is otherwise agreement on the point that SO_2 and O dried in the ordinary way, by means of concentrated sulphuric acid containing certainly a *very* slight proportion of moisture, combine much better by means of catalytic action than when the drying is not carried to the same point.]

J. P. Conroy gives a good synopsis of the theoretical and practical aspects of catalysis, containing no original matter (Journ. Soc. Chem. Ind. 1902, p. 302).

We now come to the paper by Knietsch (Berl. Ber. 1901, pp. 4093 *et seq.*), which is the most complete hitherto published on this subject. It is accompanied by a set of curves, reproduced in fig. 445, which illustrate the progress of the reaction under various conditions. Let us first take a gas, containing 20 vols. SO_2, 10 vols. O_2, and 70 vols. N_2—that is, apart from nitrogen, a stoechiometrical mixture of sulphur dioxide and oxygen. Whatever be the temperature and the velocity of the current, we see from curves S and S′ that the maximum, which always occurs at 430°, is 77 to 78 per cent. with a current of 1000 c.c. per minute, or 90 to 91 per cent. with 500 c.c. per minute. Nor can a pure mixture of SO_2 and O in Winkler's proportions, as shown in curve S″, reach a quantitative conversion into SO_3.

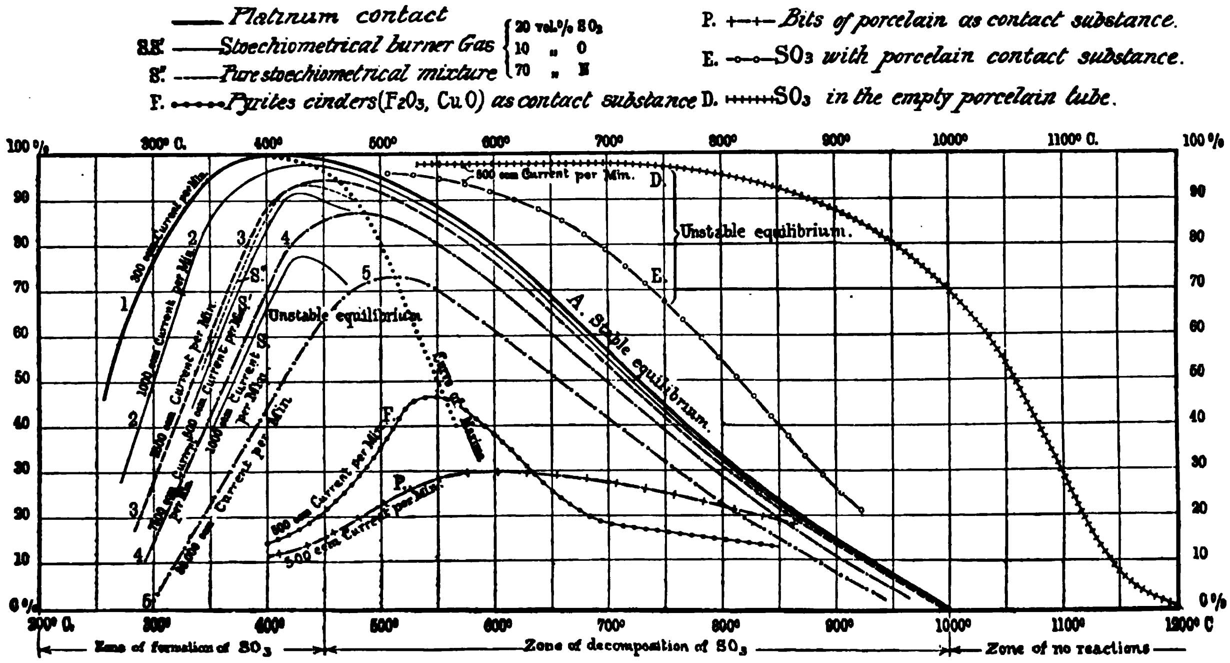
If, however, mixtures are employed in which either oxygen or sulphur dioxide is present in excess, it is possible by the action of masses of one of the constituents to displace the other constituent almost completely by converting it into SO_3. Therefore a process for manufacturing SO_3 by contact-action will go on all the better, the more oxygen is present in proportion to sulphur dioxide, the nitrogen being quite indifferent. The formula of conversion ought therefore to be written :—

$$2\ SO_2 + nO_2 = 2\ SO_3 + (n-1)O_2,$$

and n should not be less than 2.

Fig. 445.

Isochronous Reaction $2\,SO_2 + 3\,O_2 \rightleftarrows 2\,SO_3 + 2\,O_2 + 22600$ cal.



Let us now take a technical pyrites-kiln gas, containing 7 per cent. (vol.) SO_2, 10 per cent. O_2, and 83 per cent. N_2, which corresponds to about $2\ SO_2 : 3\ O_2$. Even when passing it through an *empty* porcelain tube there is some formation of SO_3; curve P shows the maximum to be 30 per cent. at 600° C.* We now fill the tube with platinized asbestos, of 5 to 10 per cent. platinum, in such a manner that the first half of the tube remains empty and serves merely to heat the gases, the other half containing about 0·5 gram platinum mixed with the asbestos. Curve No. 1, referring to a velocity of 300 c.c. per minute, shows the first trace of SO_3 a little over 200°, and a rapid increase of the formation of SO_3, which is practically complete at 380° to 400°. From 400° to 430° the quantitative action is almost constant = 98 to 99 per cent.; but then the curve descends, although more gently than it had risen, the SO_3 being more and more dissociated into its components. At 700° to 750° only about 60 per cent. of the SO_2 is converted into SO_3, at 900° to 1000° the curve reaches the zero-point.

If we repeat the experiments, changing only the quantity of contact-substance or, what comes to the same thing, increasing the strength of current, we obtain the curves No. 2 (1000 c.c. per minute), No. 3 (2500 c.c.), No. 4 (7500 c.c.), No. 5 (30,000 c.c.). These curves in their ascending branch run, for certain distances, almost parallel, but slightly diverging, which points to a common starting-point. But the descending branches all distinctly converge and ultimately all reach zero at temperatures between 900° and 1000°.

If we turn our attention to the highest points of the various curves, we observe that the maxima have a peculiar direction towards *higher* temperatures for *decreasing* quantities of platinum (or increase of velocity of the gases), and at the same time a strong decrease of the highest attainable degree of percentage conversion of SO_2 into SO_3. If these maxima are joined by a curve, marked . . . . . . in our figure, we find its left-hand portion directed asymptotically towards the theoretical maximum of 100 per cent. conversion, the right-hand portion directed towards a point near 600°.

The close approach of the curves on the side of decomposition would lead to the assumption that the dissociation of sulphuric anhydride becomes, with the decrease of platinum, more and more independent of the contact-substance and also more and more a pure function of temperature. We may test this assumption by working without any platinum, having previously brought the gaseous mixture into the state of nearly complete conversion into SO_3. This experiment was made, but yielded a very surprising result, as shown by curve D. This is shifted to the right hand by several hundred degrees, and begins to descend only at 800° to 900° C., without reaching zero even at 1100° to 1200°. This shows *that sulphuric anhydride, once formed, is very stable at high temperatures in the absence of contact-substances.* But this is an *unstable* equilibrium which is at once changed by the presence of any contact-substance and tends towards a *stable* equilibrium. Curve E shows this influence, consisting in a gradual approach of curve D to A, when repeating the experiment as at D, but with a tube filled with pieces of porcelain. This reminds one of the phenomena of superfusion and retardation of boiling, and at such temperatures porcelain and other substances prove to be similar catalyzers to platinum. But it seems extraordinary that at such temperatures, viz. a vivid red-heat, such a strong retardation in reaching a stable equilibrium takes place.

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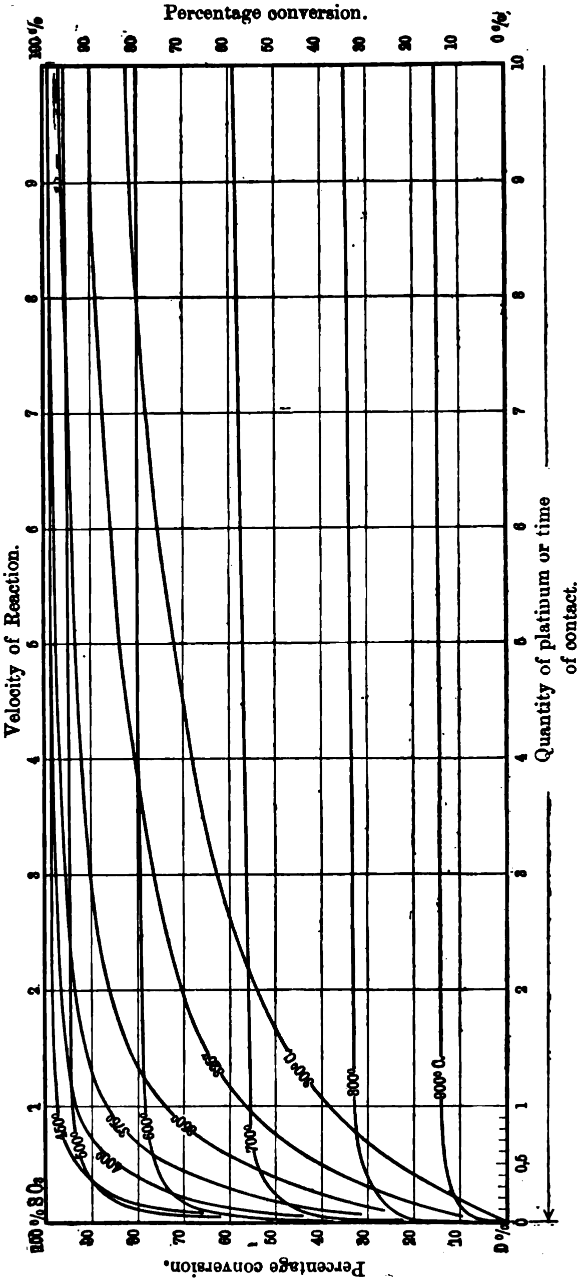
* Comp. above pp. 979 & 980, the attempts at forming SO_3 by merely heating the roasting-gases in flues filled with pebbles, &c.

Bodenstein (Chem. Zeitg. 1902, p. 1077) holds that the preceding observation of Knietsch, according to which the porcelain contact does not form SO_3 so easily as platinum contact, but does not destroy the formed SO_3 in the same ratio, is a simple case of thermodynamics.

We have seen above that the reactions plotted in curves 1, 2, 3, 4 are dependent upon the duration of the contact of the gas with the contact-substance. This is made clearer by the curve fig. 446, where on the X-axis the times of contact or, what comes to the same thing, the quantity of platinum is plotted, on the Y-axis the percentage proportion of SO_2 transformed into SO_3. We perceive from this curve at once what time or what quantity of platinum is required for a certain percentage formation of SO_3 for a definite temperature. We also perceive that the curves begin at zero and run asymptotically parallel to the X-axis, tending towards the maximum corresponding to the temperature. We also see that with the increase of temperature and the percentage increase of SO_3 the curves get more and more bent, but more and more removed from a perfect transformation. Ultimately the velocity at commencement is so great that at higher temperatures the

Fig. 446.

Isothermal Reaction $2\,SO_2 + 3\,O_2 \rightleftarrows 2\,SO_3 + 2\,O_2$.



beginning of the curves almost coincides with the Y-axis. Hence the first meeting of the roasting-gases with the contact-substance must lead to a violent reaction, and therefore to a strong heating of the first portions of the contact-substance, which, according to the kind of external coaling, may go up to a visible glowing.

We see further from the curves that with the formerly generally employed temperature of the contact-furnaces the reaction could not possibly be quantitative, and that it is only the sulphur trioxide itself which strongly retards the velocity of the reaction.

The most important result of Knietsch's experiments was that a line of *stable* equilibria exists which divides the range of temperature into two parts. The ranges below 200° and above 900° or 1000° may be called devoid of reaction in a technical sense; between 200° and 450° the reaction of formation prevails, above 450° the dissociation of SO_3 comes into play very rapidly.

From these facts important technical conclusions may be drawn. Although the limiting line A (fig. 445) has been worked out only for a certain technical mixture of gases, we may safely assume that the different practically important cases will not have very much influence on the *position* of this stable equilibrium. This limiting-line must theoretically and practically be independent of the kind of contact-substance; hence only those contact-substances will be able to produce a quantitative reaction in *one* operation which exhibit the maximum of activity below 450°. All contact-substances which exhibit their maximum activity only beyond that temperature (such as pyrites-cinders containing Fe_2O_3 and CuO, comp. curve F, p. 1002) will never be able to produce a quantitative conversion of SO_2 into SO_3, whatever the length of time that may be employed. Hitherto only one substance has been found to fulfil the necessary conditions, viz. platinum, which cannot be replaced by any other member of the same group of metals with even approximately similar success.

The preceding conclusion of Knietsch has been hitherto justified by the fact that notoriously in those places where ferric oxide, whether in the technically pure state or mixed with other oxides, is employed, the conversion never even approximately reaches 100 p. c., but only 60 to 66 p. c., and the end of reaction is brought about by a second passage over platinum black. The theory of the contact-action of ferric oxide has been touched upon before (pp. 997 *et seq.*). From the factories where it is actually employed no experiments have been published thereon, but an experimental investigation on that point has been made by the author, together with G. P. Pollitt, which will be subsequently mentioned.

We shall find further contributions to the theory of platinum catalysis in the original communication of Dr. Krauss, of Höchst, to be given later on.

Brode, in the paper mentioned in Chap. VII. p. 775 (Zsch. angew. Ch. 1902, p. 1081), quotes the views of Krauss, as shown in the British patents of 1901, with full approval. We shall in this place give merely a short extract from Brode's paper. The catalytic action of platinum in the reaction $SO_2 + O = SO_3$ is technically applicable between 400° and 500°. But already at 400° the counter reaction sets in and is almost complete at 1000°. Although, therefore, a higher temperature would increase the velocity of the formation of SO_3 (at 500° it is 200 times as strong as at 400°), the equilibrium is shifted to the detriment of the product desired. Practically it is impossible to work at the temperature at which the reaction is complete, because the velocity would be too small. In order to combine the highest velocity with a nearly quantitative yield, we must draw the consequences of the law of the action of masses; that is, we must either increase the concentration of the substances to be changed, or lower the concentration of the product to be obtained. The former cannot be done at will; the SO_2 is given, and merely the oxygen may be concentrated by employing more air, as the Mannheimer Verein has prescribed in their respective patent (see below). It is, however, not feasible to go too far in this direction, both from practical and theoretical grounds, at least not when working with atmospheric air, where any raising of the concentration of oxygen beyond 17 p. c. (with 3 p. c. SO_2 and 80 p. c. N) would have but a very slight effect, the yield being proportional to the square root of the concentration of oxygen. It is therefore proper to proceed in the other direction, that is, *to lower the concentration of the product obtained*, SO_3, by taking it away by continuous or successive absorption. In this case the equilibrium is constantly disturbed, the reaction recommences, and ultimately all SO_2 is changed into SO_3, even under unfavourable conditions of equilibrium. Hence we need not work at the optimum temperature of 450°, but, if proceeding as indicated, we may go considerably beyond that, and we shall then do far more work in a given apparatus in the same time, and we may also then employ catalyzers which act only at higher temperatures. The first action will be best performed at high temperatures and correing velocities, and when the equilibrium has been reached, lower temperatures will be applied in order to perfect the yield.

From a paper by G. Lunge and G. P. Pollitt, in Journ. Soc. Chem. Ind. 1903, p. 79, on the formation of sulphur trioxide by the action of ferric oxide, I quote only the conclusions :—

(1) The degree of change of SO_2+O to SO_3 is not sensibly affected by changes in dilution from 2 to 12 per cent. of SO_2 by volume. A still greater dilution would probably act equally well (*vide* Sackur's theoretical observations, *suprà*, p. 1000). Above 12 per cent. the percentage change is not only lowered, apparently because of the too small excess of oxygen, but also the contact-action of the oxide is made worse for more dilute mixtures.

(2) The mixture of gases to be changed to SO_3 must be as dry as can be obtained by a thorough treatment with sulphuric acid. The neglect of this precaution not only causes the contact-action to be at once much lessened, but, in addition to this, the contact-mass has to be treated for a long time with the dry mixture before it recovers from the "poisoning" action of the moisture.

(3) Exactly the same results are obtained as by treating with moist gases when oxide of iron (pure or containing copper) which has been exposed to the air, and has therefore absorbed some moisture, is used. Only after long treatment with the gases at red-heat (lasting 30 hours or more) does the oxide of iron reach its maximum contact-action, which, however, immediately sinks again if the oxide after cooling is even for a short time exposed to the air.

(4) An improvement of the contact-action by methods of treatment having for their object the loosening of the surface of the oxide of iron was not achieved. Oxides obtained by heating ferri- or ferrosulphate gave a much lower contact-action than that obtained with an oxide prepared by igniting precipitated hydroxide, or in the form of pyrites-cinders. Doubtless the physical formation of the oxide has a great influence on its catalytic action, but we have not so far succeeded in clearing up this point.

(5) An addition of copper oxide to the iron oxide (using the cinders from pyrites containing copper) is favourable to the formation of SO_3.

(6) Arsenious acid is completely taken up and retained by oxide of iron at a high temperature. (The best temperature seems to be not less than about 700° C.) The oxide of iron can be thus charged with arsenic up to considerable quantities. An oxide thus charged,

if it contains 2⅗ per cent. of arsenic (reckoned as As), shows a very considerably increased contact-action (over 60 per cent.) in comparison with the pure oxide.

(7) Oxide of iron containing copper also shows a distinct increase of contact-action on being charged with arsenic.

(8) The best temperature for the catalytic action of ferric oxide in the formation of SO_3 lies between 600° to 620° C. Below 600° the action is very slight; above 620° the catalytic action falls quickly to a certain point and remains constant till 750°, when it again begins to fall. The fall on raising the temperature must be attributed to the fact that the system $SO_2 + O \rightleftarrows SO_3$ tends to alter its condition of equilibrium, in the direction from right to left, on raising the temperature. The fact that there is no appreciable change between the temperatures of 635° and 750° can perhaps be best explained by assuming that two kinds of intermediate reactions come into play, viz.: first, the formation and decomposition of ferrisulphate; and, secondly, the alternating reduction of Fe_2O_3 and oxidation of the Fe_3O_4 so formed, and that these reactions have different temperature optima.

I have been favoured by Dr. Brode, of Karlsruhe, with the following remarks on the maximum yield theoretically obtainable in the manufacture of SO_3 by the contact method. From the graphic representation given by Knietsch (p. 1002), it appears that he had obtained from technical burner-gases the equilibrium $2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$ at temperatures over 450° C., since the yield did not change after some time or when employing more contact-substance. At lower temperatures the yields were still gradually increasing, and hence the equilibrium was not yet reached. As Knietsch worked with gases containing 7 per cent. SO_2, 10 O_2, and 83 N_2 by volume, we can calculate the equilibrium constant K for temperatures upwards of 450° by the formula:

$$K = \frac{[SO_3]^2}{[SO_2]^2} \frac{1}{[O_2]},$$

and we thus arrive at the following table, in which column I. shows the temperatures; II. the yields obtained by Knietsch (as read off from the curves); III. the proportion $SO_3 : SO_2$ calculated therefrom; IV., V., VI. the concentrations of the single gases at equilibrium, expressed in per cent. by volume; VII. the constant, expressed in the same way.

I. ° C.	II. Yield $\frac{100\,SO_3}{SO_3+SO_2}$.	III. $\frac{[SO_3]}{[SO_2]}$.	IV. SO_3 per cent. vol.	V. SO_2 per cent. vol.	VI. O_2 per cent. vol.	VII. Const. K.
450	98 p. c.	49	6·86	0·14	6·6	364
500	95 „	19	6·65	0·35	6·7	54
600	80 „	4	5·60	1·40	7·2	2·2
700	59 „	1·40	4·13	2·87	7·9	0·25
800	35 „	0·54	2·45	4·55	8·8	0·033
900	15 „	0·18	1·05	5·95	9·5	0·0034

The constant now allows us to calculate the maximum yields obtainable at given temperatures and concentrations of oxygen for the case that the equilibrium is actually obtained, and independently of the contact-substance (according to van't Hoff, Vorles. chem. Dyn. p. 211). For each temperature the relation is:

$$\sqrt{K[O]_2} = \frac{[SO_3]}{[SO_2]},$$

and the percentage yield:

$$\frac{100[SO_3]}{[SO_3]+[SO_2]} = \frac{100\sqrt{K[O_2]}}{1+\sqrt{K[O_2]}}.$$

In the subjoined table, column I. shows the results obtained experimentally by Knietsch with technical burner-gases containing 7 vol. per cent. SO_2, 10 O_2, 83 N_2; II. the yields theoretically obtainable by the process employing great excess of air, assuming the concentration of oxygen at equilibrium = 16 vol. per cent. O_2; III. the yields obtainable by burning sulphur in pure

Temp. ° C.	I. Technical burner-gas.		II. Burner-gas with excess of air.		III. Burning S with pure oxygen.	
	$\frac{SO_3}{SO_2}$.	Yield per cent.	$\frac{SO_3}{SO_2}$.	Yield per cent.	$\frac{SO_3}{SO_2}$.	Yield per cent.
450	48	98	76	98·7	181	99·5
500	18	95	29·3	96·7	70	98·6
600	4	80	5·8	86	14	93
700	1·4	59	2·0	67	4·7	81
800	0·54	35	0·73	42	1·7	62
900	0·18	15	0·23	19	0·55	36

oxygen, the gases showing 7 vol. per cent. SO_2 and 93 O_2, and the oxygen concentration = 90 per cent. at equilibrium.

Keppeler (Zsch. f. angew. Ch. 1902, p. 809) has made some interesting observations on the conditions to be fulfilled by every contact-substance. Apart from the property of forming two grades of oxidation, of which the higher is reduced by SO_2 at the same time as the lower is oxidized by O (comp. p. 999 respecting this property even in the case of platinum, according to Engler and Woehler), those substances which form sulphates, like ferric oxide, must be considered in another respect as well. On heating sulphates they begin to throw out molecules of SO_3 in a proportion increasing with the temperature; and for each temperature they continue to do this until the vapour of SO_3 in the space above the sulphate has a tension equal to that with which the SO_3 is split off from the oxide. If that equilibrium is disturbed by the change of atmosphere, the sulphate again splits off SO_3, and this goes on until only oxide remains. Hence it is unnecessary to work at a temperature at which the dissociation of the sulphate is complete, that is, until the tension is equal to that of the atmosphere. It is only necessary that the partial pressure of the vapour of SO_3 should be less than the tension of dissociation of the sulphate at that temperature. With the dilution of the burner-gases the temperature is lowered at which the contact-substance is active. If, for instance, the burner-gas can furnish 8 per cent. SO_3, a temperature suffices at which the SO_3 vapours split off by the sulphate have a tension of 0·08 atmosphere. At 400° the SO_3 tension of ferric sulphate is not sensible; it becomes so at 500°, and probably it is not necessary to exceed that temperature largely if very dilute gas (2 to 3 per cent. SO_2) is employed, because then the temperature required for the formation of sulphate is much lower: the excess of oxygen is useful through the action of the law of masses, and the heat of reaction, being applied to a greater mass, does not produce a harmful rise of temperature.

PRESENT STATE OF THE MANUFACTURE OF SULPHURIC ANHYDRIDE AND SULPHURIC ACID BY THE CONTACT-PROCESS.

This process is carried out in practice in a considerable number of modifications. About some of these nothing whatever is known outside the circle of those who work them, and concerning these I can naturally say nothing in this place. To this number belong the processes used by Messrs. Chapman, Messel, & Co., at Silvertown, by the United Alkali Company and by the Tentelew Chemical Works at St. Petersburg [comp. a description of their apparatus in the B. P. No. 11,969, of May 26, 1902, Journ. Soc. Chem. Ind. 1903, p. 695).

Only six different processes are better known, partly by the patent specifications and partly by communications from the owners, most of which appear for the first time in this book. We may divide them into two classes:—

A. Processes by which the conversion of SO_2 into SO_3 is rendered practically complete by contact-action (Badische, Höchst, Grillo, Mannheim).

B. Processes which supplement the contact-process by ordinary lead chambers for working up the residual gases (Freiberg, Rabe).

I. *The Process of the Badische Anilin- und Sodafabrik at Ludwigshafen.*

British patents: Nos. 15,947, 15,948, 15,949, and 15,950, all of July 21, 1898; No. 1904, Jan. 28, 1901; Nos. 6828 and 6829, April 1, 1901; No. 12,781, June 22, 1901. U.S. patents (Knietsch): No. 690,062, Dec. 31, 1901; No. 692,018, Jan. 28, 1902; G. P. No. 142,895, June 4, 1902.

This process has been worked out by Dr. Knietsch, who has described its rise and present state in a lecture delivered before the German Chemical Society on Oct. 19, 1901, which has been published in Berl. Ber. 1901, pp. 4078 *et seq.*

The whole of the matter contained in that lecture, as far as it refers to the subject in question, is given in the following description, which is, however, largely amplified by extracts from the patent specifications and by a direct communication made to me by the Ludwigshafen firm.

When Knietsch approached the problem of completely converting pyrites-kiln gases into sulphuric acid by contact-action, this seemed to promise no success according to all that was known at that time in practice and theory. He was induced, in spite of this, to consider success possible principally from theoretical considerations.

We know that the gases issuing from the ordinary lead chambers still contain 6 per cent. oxygen. The same excess of oxygen must necessarily be present in every burner-gas submitted to the contact-process, and there was no apparent reason why the reaction should not go on quantitatively with such an excess of oxygen. This question was tested by experiments with pure sulphur dioxide diluted with much air, and it was found that the reaction under certain conditions stopped quite short only of quantitative conversion. It was found that dilution with air to any extent had next to no influence on the conversion of SO_2 into SO_3, nay, even that this conversion was promoted by diluting the SO_2 with more air and thus increasing the proportion of oxygen in comparison with dioxide. From this followed the fact that the view held up to that time, according to which diluting gases had an injurious effect on the contact-process (comp. p. 985), had to be critically examined.

The experiments were now extended to real burner-gases, taken from the pyrites-kilns and conducted to the laboratory through a long lead tube, acting like a flue-dust chamber in removing cinders, flue-dust, &c. The gases were also washed by several bottles charged with sulphuric acid. The results were almost as complete as those obtained with artificial mixtures of gases, and no falling off in the quantitative action was observed, although the experiments with the same contact-mass lasted several days.

This seemed to justify the hope that sulphuric acid might be almost quantitatively made in this way from burner-gases, and the experiments were repeated on the large scale; but it was soon found that the action of the contact-substance did not hold out during a prolonged use and ultimately it entirely failed. This result was not improved by cooling the gases in long flues and repeatedly washing them with sulphuric acid, nor by filtering them through dry coke and asbestos filters so that they might be regarded as pure as could be technically attained. So far, the process had failed on the large scale. But on making further laboratory experiments on the causes of the slow, but seemingly inevitable, retrogression of the contact-action it was found that some substances interfere with the catalytic action of platinum even when present in extremely small quantities. These are arsenic and mercury, also phosphorus, but later on the injurious effect of the latter was found to be caused by its contamination with arsenic. Other substances, such as antimony, bismuth, lead, iron, zinc, &c., are injurious only so far as they mechanically envelop and stop up the contact-mass, if introduced in large quantities. The injurious effect of arsenic is so great that 1 or 2 per cent. of the weight of platinum suffices for depriving this entirely of its activity.

The question now arose, whether those "contact-poisons," as they may be styled, are present in burner-gases after all the purifying operations above described, and it was found that indeed the whitish mist of sulphuric acid, which could not be precipitated, contained arsenic. Thus the want of success was partially cleared up, but no remedy was known, since up to that time the *complete* precipitation of these white mists was considered technically impossible by the most competent experts (*cf.* Schnabel's 'Hüttenkunde,' 1890, p. 500). Still, the task was again taken in hand to accomplish a complete removal of *all* impurities, so as to leave a mixture of absolutely pure sulphur dioxide, oxygen, and nitrogen. An enormous amount of time, trouble, expense, and patience was required for attaining that object, first in the laboratory, and then on the large scale. The difficulty was principally caused by the continuous struggle with an *invisible* foe, and the fact that each mistake was attended by a lasting diminution of the yield of the whole plant. The result of the whole work is embodied in the patents cited above, p. 1012, which show that the burner-gases can indeed be completely freed from all impurities, if, after proper treatment and cooling, they are subjected to a prolonged systematic intimate contact with water or sulphuric acid, carried on until an optical and chemical examination proves their perfect purity. It is indifferent for the result in which way that intimate contact with the purifying liquids is attained, whether by intense washing or wet filtration, or a combination of both. Only a few of the difficulties will be mentioned which occurred during the introduction of the purifying process into practical work.

It was found that the gases should be *slowly* cooled, in which case the sulphuric-acid mists are much more easily precipitated than when cooling rapidly (say, by bringing them into contact with much water)—a phenomenon which may be caused by different states of the sulphuric anhydride (p. 162), but still awaits its proper explanation (comp. also p. 981). The cooling required long *iron* conduits cooled by air. So far as was then known, the iron could not have any injurious effect, for acid with more than 90 per cent. H_2SO_4, such as must be formed when dry pyrites is employed, was not expected to act upon iron, or to yield at most SO_2, which could do no harm. But although the burner-gases had been completely purified, and even passed through wet filter-presses, and the optical test (then regarded as sufficient) betrayed no contamination, yet the contact-mass was slowly, but infallibly, changed after weeks or months. After a long series of investigations, and only after the presence of arsenic, undiscoverable in the gases, had been proved in the platinum asbestos after having lost its activity, the assumption gained ground that the disturbance might arise from an attack of the small quantity of sulphuric acid condensing in the iron cooling-pipes, and that this must proceed from the formation of a gas containing arsenic, presumably arseniuretted hydrogen. Precautions were now taken that the condensing acid should not come into contact with iron, and from this moment the contact-furnaces retained their activity without any change. Consequently, contrary to the general view up to that time, the action of concentrated sulphuric acid on iron must have produced some hydrogen, for only in this way arseniuretted hydrogen could have been formed.

Another very enigmatical and protracted disturbance arose through the formation of mists in the pyrites-kilns, after lengthy investigation discovered to be very slight mists of unburned sulphur, which is just as difficult to precipitate as a quickly cooled mist of sulphuric acid. This sulphur always contained some arsenic, and had therefore to be completely removed ; this was attained by thoroughly mixing and thus completely burning the gases by the assistance of blowing in some steam. This has another very important advantage by diluting the sulphuric acid present in the gases so that it does not condense in the first iron coolers (which prevents the formation of AsH_3), nor attack the subsequent lead coolers when condensed to liquid acid; it also prevents the formation of hard flue-dust and obstructing crusts in the flues and coolers.

In the patents the purifying process is described as follows :—The hot gases are treated with a jet of steam in the dust-flue; they are then gradually cooled by being passed through a flue and then into a set of lead pipes, arranged to act as a cooler, where the temperature is lowered to about 100° C. They are then passed through a series of mechanical washers, the water in which becomes converted into dilute sulphuric acid. Such washers act incomparably better than washing-towers. The gases are finally dried by concentrated sulphuric acid. Before they pass on to the contact-apparatus, they are subjected to an optical and a chemical test. The former consists in examining a layer of the gas some yards in length, illuminated at the further end, to see that it is free from dust and mist. The chemical test is performed by passing the gas for 24 hours through water and then examining the liquid by the Marsh test for arsenic.

We now come to another important principle of the Badische system, *the removal of the injurious excess of the heat of reaction.* The process $SO_2+O=SO_3$ produces 22,600 calories. In Lunge's 'Sulphuric Acid and Alkali,' 2nd edition, vol. iii. p. 815, the following paragraph occurs:—"At a large German works pure SO_2, obtained by the Schröder and Hänisch process, or in some other way, is mixed with the necessary quantity of air; the mixture is heated to the required temperature in a pipe-stove, and is then passed through an apparatus containing clay-balls impregnated with platinum black, similar to a Deacon decomposer. This apparatus requires no external heating, since the gaseous mixture develops heat in the combination of SO_2+O, and needs only to be protected from cooling. It is asserted that, by employing strong pressure by means of bronze blowing-engines (air-compressors), it is possible to make SO_3 directly from pyrites-burner gas cheaply enough to employ it for bringing chamber-acid up to the strength of 'rectified oil of vitriol,' in lieu of concentration by evaporation, or even to manufacture ordinary sulphuric acid in this way, and thus to do away with lead chambers."

But this refers to a highly concentrated mixture, containing about 25 per cent. (vol.) of SO_2, and could not be applied to gases three or four times more diluted. Such gases were universally believed to require not merely protection of the contact-apparatus from cooling, but heating it up to red-heat. Consequently the apparatus at the Badische was first provided with a heating arrangement. It was formed of vertical pipes, somewhat narrow, as in these the platinized asbestos can be more uniformly distributed than in wider, horizontal pipes or boilers.

The contact-furnace hence consisted of a bundle of narrow pipes, the lower half of which was filled with contact-substance, as shown in fig. 447 (taken from the patent specification). When this furnace was started in the ordinary way at a low red-heat, it was found, against all expectations, that not merely the yields were better, but the velocity of the gaseous current could be essentially increased, if, in lieu of hot fire-gases, *cold* air was introduced between the pipes and the temperature loss thus kept essentially lower. This led to another way of proceeding. In the beginning the two fires *h* and *h'* were used, but as soon as the furnace was at work, the lower fire *h* was put out and cold air was passed along the contact-pipes, thus both cooling the pipes and performing a preheating of the cold gases entering the pipes by means of the heated current of air rising up; the fire *h'* had only to complete this preheating. In this way only the upper layers of the contact-mass became gently red-hot, and a proper temperature for the completion of the reaction was attained throughout.

In this simple manner the work was performed for several years; the temperature can be noted without a pyrometer by merely observing the appearance of the bundle of pipes. But it was found later on that the quantity of heat which could be withdrawn from the contact-process was so great that it is possible to employ the roasting-gases themselves as cooling-gas and thus to utilize the excessive heat of reaction for heating up the cold roasting-gas. This is done in the apparatus shown in fig. 448, where the arrows indicate the way which the gases take.

Fig. 447.

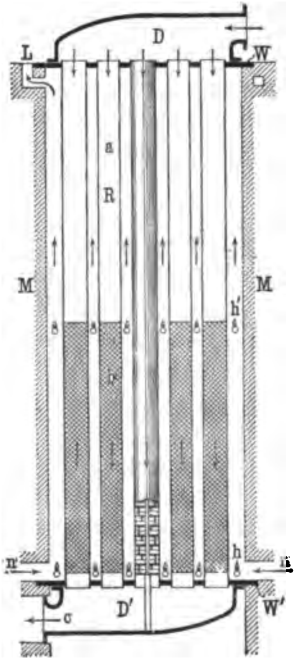
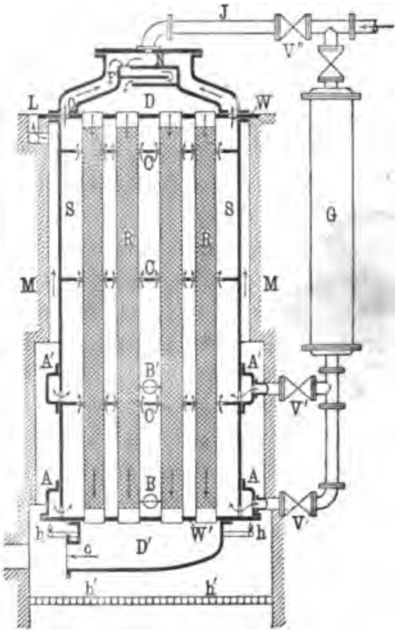


Fig. 448.



Within the brickwork M M an iron cylinder S S is arranged, with top cover W and bottom piece W′, and pipes R R passing through the diaphragms D D′. The whole can be heated up to the temperature of reaction by a fire &c. at *h h′*; the gases of this fire escape at L. The burner-gas to be treated passes first through the heat-regulator G, then through the valves V V′ into chambers A and A′, which supply the whole circumference of S with gas, as well as the radial pipes B B′, which are provided with holes of a size varying according to the length of the corresponding chord of the circle, so that the gas is divided uniformly all over the system.

In order to lead the gases further on in the requisite way and to bring them as near as possible to the contact-mass to be cooled, a number of diaphragms C C are provided, which force the gases to travel close to the pipes R R. The gases are again thoroughly mixed before entering into these pipes through O and F, and acting upon the mass by means of the baffle-plates in chamber N.

The velocity and temperature of the gaseous current is regulated by thermometers placed at D and D′, and by analysis of the entering and issuing gases, until these yield the best results. If needful, other cooling-gas or air may be admitted through V″ and J. In pipes R R the contact-reaction takes place, the heat generated in excess being transferred to the gases playing round these pipes, which are thereby heated up to the temperature of the reaction. The transformed gases issue through D′ into chamber W′ and proceed through G to the absorbers; but they may also be carried through the heat-regulator G, where they give up part of their heat.

The patent specifications contain a number of other forms of apparatus for applying the same principle.

There is also a specific example quoted to show how the best result can be obtained, but this applies to gases not obtainable from ordinary pyrites-burners, viz. such containing 12 per cent. (vol.) SO_2 and 12 per cent. O. The apparatus is heated up by the gas-flames at *h* until the thermometer in D shows 300° C., and the whole gaseous current is now allowed to enter at A. By constantly testing the entering and issuing gas the practical effect is ascertained, and the temperature in the contact-space, which is observed by thermometers in D and D′, is regulated by means of admitting the cooling gas through valves V, V′, and V″, if necessary by help of the preliminary heater G, under such conditions of heat and quantity that the maximum conversion of SO_2 into SO_3 is attained. In the present case about two-thirds of the gas is introduced at A and one-third direct through J, so that, after passing the mixer N, the gas in D shows a temperature of

380°, the thermometer in D′ showing 234°. The conversion of SO_2 into SO_3 is = 96 to 98 per cent., if 40 to 50 kil. SO_3 are made for each pipe in 24 hours ; the yield may rise to 99 per cent. if the gases are left in contact with the catalyzer for a longer time.

This cooling system furnishes four important advantages :— 1. There is no overheating of the apparatus, and a temperature is obtained suitable for the highest possible yield of 96 to 98 per cent. 2. The iron apparatus is protected from being destroyed by burning. 3. The contact-mass is protected from overheating and retains its activity for years. 4. The absolute amount of work done by the contact-mass, and therefore by the whole apparatus, is very considerably increased and brought to its upper limit, because fresh quantities of gas can always be introduced without overheating and the contact-mass is kept at a temperature most suitable for its maximum effect. Hence, if the furnace gets too hot, it is not necessary, as before, to diminish the gaseous current to be treated, but its cooling action is regulated by changing its quantity or its temperature when entering the cooling-jacket, or the place where it enters, &c.

An essential point in the new process is that it is carried on without applying high pressure. Formerly it was believed (p. 993) that the influence of indifferent gases militated against quantitative action and that this should be compensated by employing the gases in a highly compressed state. But such an influence is absent or at least practically *nil.* There is no difficulty whatever in reaching an almost quantitative conversion of SO_2 into SO_3 without any excess pressure, which means a considerable saving.

On the other hand, the gas should be made to penetrate the contact-mass very thoroughly. Loose platinum asbestos gets easily compressed too much to allow the gases to penetrate. The apparatus shown in fig. 449 allows of working with a minimum of pressure without leaving the gases any other way except through the contact-mass itself, or hindering the cooling of the contact-pipes. The contact-mass is spread on perforated plates, strung on a central round iron spindle; small bits of pipes or pins keep the single plates apart and prevent the pressure of one layer upon another, so that there is but very little resistance to the gases, and a correspondingly small mechanical force required for propelling them. Each pipe can also be brought to a certain pressure, uniform for all of them and capable of being measured, so that the whole apparatus, although consisting of many pipes, offers an absolute guarantee for a uniform division of the gases and therefore the most normal progress of the reaction.

The best way of performing the above is described in G. P. 119,059. Pipe R (fig. 449) contains a central spindle *a* resting on the bottom of the apparatus and serving as guide for the following parts. On this is put a pipe *b*, reaching into the contact-pipe. Upon this is dropped a perforated plate or sieve *c*, upon which enough contact-mass is spread to cover not merely the holes, but also the space between the edge of the sieve and pipe R. Now a small bit of pipe *d* is dropped over *a*, on this again a perforated plate *c′*, and this is continued until there is enough contact-substance in the pipe. Or else, in lieu of pipes *d*, the sieve-plates are kept apart by small tripods, as in fig. 450.

Fig. 449.

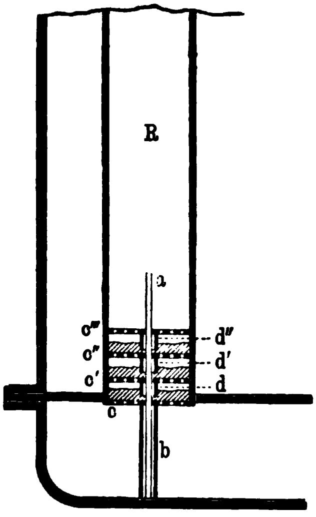
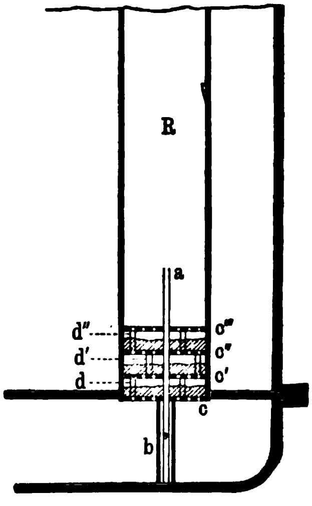


Fig. 450.



A recent patent of the Badische (E. P. 6828, of 1901) describes the formation of a "carrier" (in place of asbestos) by the intermediate action of an intimate mixture of an oxide or hydrate of a fixed alkali or alkaline earth, or salts of these containing a volatile acid (HCl, CO_2, acetic acid, &c.), with a salt of a volatile base, such as ammonia, and a more difficultly volatile acid, such as sulphuric or phosphoric acid, at a suitable temperature. At such a temperature double decomposition takes place, and the vapours of the volatile salt so formed on escaping impart a high degree of porosity to the non-volatile salt remaining behind. The platinum may be added to the mass either before or after heating.

Another recent patent of the same firm (No. 12,781, June 22, 1901) states that half of the platinum or more, up to 70 per cent., can be dispensed with by dividing the process into two stages, and removing the SO_3 formed in the first stage before submitting the gases to the second stage. Otherwise, with 100 parts of platinum and a total conversion of 97 per cent., the production of the first 80 per cent. SO_3 only requires 15 parts of the total platinum employed, while for the remaining 17 per cent. SO_3 85 parts of platinum are necessary. But if, after in the first phase converting 80 per cent. of the SO_2 into SO_3, the latter is removed by absorption and the remaining gases are again submitted to contact-action, the formation of SO_3 proceeds again with the same velocity as at first, so that the total conversion is $= 80 + \left(20 \times \frac{80}{100}\right) = 96$ per cent. This is sufficient for practical purposes, and it takes only $15 + 15 = 30$ parts of the platinum necessary for a direct conversion of 96 per cent. In the same manner it is possible to rise from 80 per cent. in the first phase to 98 per cent., or from 90 per cent. in the first phase to 99 per cent. total conversion.

A further patent of the same firm (G. P. 142,895) shows how the spent contact-substance may be regenerated by passing through it inert gases, mixed with vapours of HCl, SO_2, &c., until the impurities have been removed.

Last of all we must allude to the question of *absorbing* the sulphur trioxide contained in the gases. It is well known that SO_3 has much more affinity to water than to concentrated sulphuric acid; in the former case 1 kil. SO_3 liberates 500 calories, in the latter (1 kil. SO_3 with an excess of sulphuric acid 66° B.) only about 300 calories. It would therefore be the most natural thing to arrange a number of vessels in such manner that the absorbing acid is gradually less concentrated in the direction of the gaseous current, that water or dilute acid is run into the last vessel, and that fuming acid or acid of any other desired commercial concentration is run out from the first vessel. Against all likelihood such an arrangement does *not* produce the maximum of work. On the contrary, it is very difficult to absorb SO_3 by means of water or dilute sulphuric acid; considerable quantities of whitish mist still escape from the apparatus, causing loss (and nuisance). But it has been found that at a certain concentration, between 97 and 98 per cent. H_2SO_4, sulphuric acid has the property of absorbing sulphur trioxide completely and momentarily. (This peculiar property of acid of that special concentration, together with its other remarkable properties, has been described on p. 175, where also Sackur's explanation of the phenomenon described by Knietsch is given.) It is thus possible to remove all the SO_3 out of the gaseous current by a single absorbing-apparatus, in which the concentration of the acid is kept between 97 and 98 per cent. H_2SO_4, by continuous feeding with water or dilute acid, and continuous running off of the excess of strong acid formed.

If *fuming* acid is to be made, one or more absorbers are placed in front of the last. Here again very peculiar phenomena are observed. Whereas in the manufacture of hydrated sulphuric acid cast-iron vessels are very suitable, this is not the case with fuming acids, which do not corrode the cast-iron very much, but cause it to crack (comp. p. 206). Wrought-iron is strongly corroded by fuming acids of less than 27 per cent. SO_3, as is explained by its electric conductivity (p. 175). Above 27 per cent. SO_3 the acid renders wrought-iron entirely passive, and such apparatus can be used for many years for the manufacture of *strongly* fuming O.V., above 27 per cent. SO_3. Thus also fuming acid almost entirely free from iron can be made (0·003 to 0·001 per cent. Fe).

The American patent of R. Knietsch, No. 692,018, of Jan. 28, 1902, contains a synopsis of the various operations, and is shown in fig. 451. Sulphur dioxide is taken from the supply A through the drying-train B into the "induction separator" C, in which the gas is mixed with air from the pump D; the mixed gases then enter the washer E, a leaden vessel from the top of which is suspended a hood having serrated edges dipping into sulphuric acid of 66° B.; a pressure-gauge affixed to the entrance and another to the exit show the respective pressures. The gases then pass through the "stripper" F, similarly formed to the washer, but containing no liquid except such sulphuric acid as may be deposited by the gases, which next enter the contact-chamber H and then the absorber I of wrought-iron (having a serrated suspended hood of the same metal containing sulphuric acid of 66° B., which thus becomes fuming acid by absorption of SO_3). The absorber I is immersed in a cooling-vessel. The second absorber J is of a similar construction, but is made of cast-iron; it contains sulphuric acid of 58° B., which, when brought up to 66° B. by the SO_3 reaching

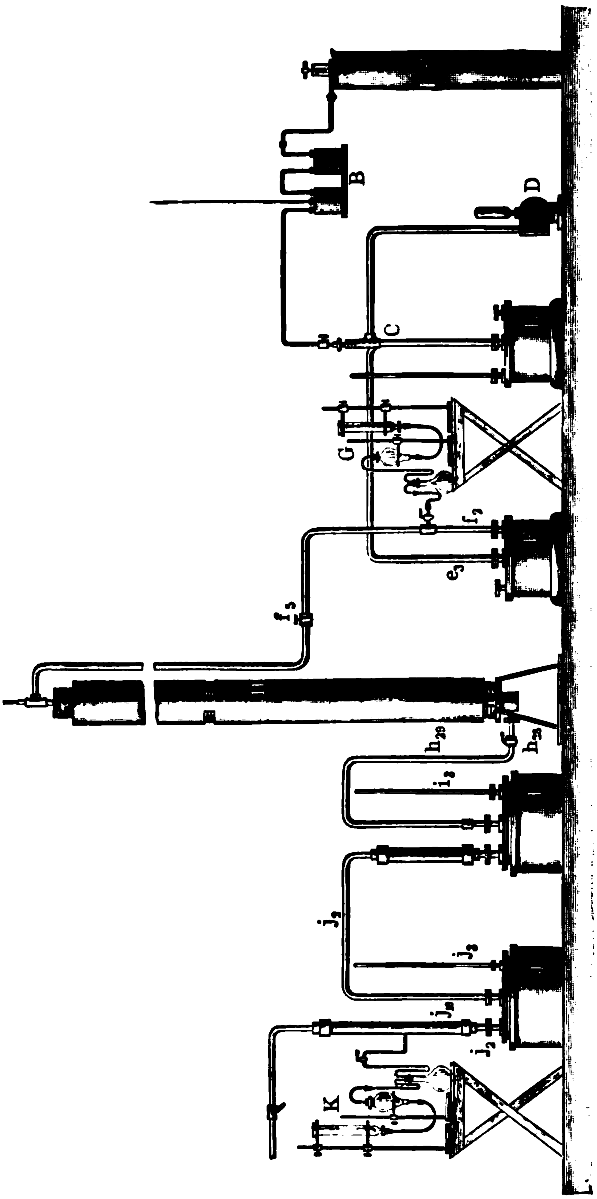


Fig. 451.

it, is available for recharging absorber I. G and K are testing-apparatus.

The contact-furnace H is separately shown in fig. 452. 1 is a central tubular contact-chamber, jacketed by the annular passage 2 and surrounded by insulating material 4. The sheet-iron tube 3, forming the annular passage, is pierced to form a series of port-holes, 14, 15, and 16, each series being provided with two independent semicircular covers, 38, 39, and 40, governing separate halves of the series, by which admission of air for regulating the heat is

Fig. 452.

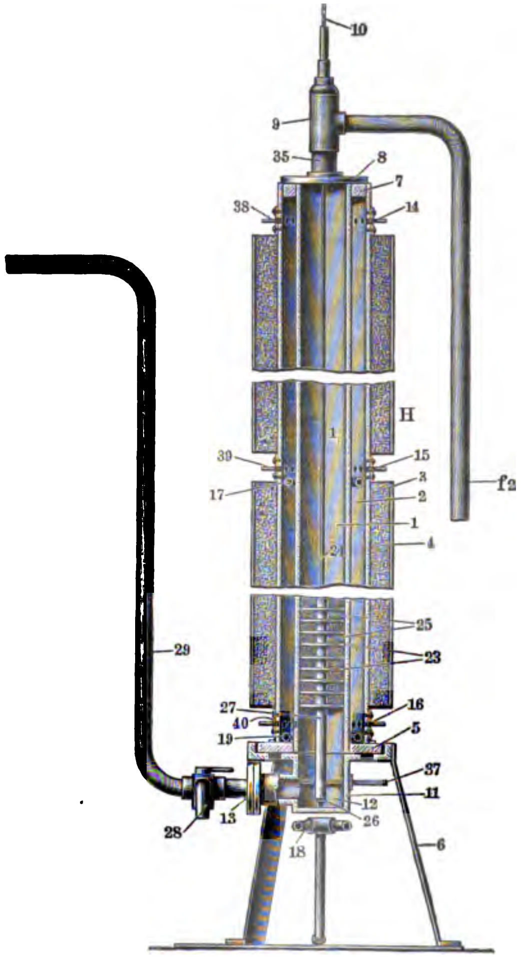


Fig. 453.

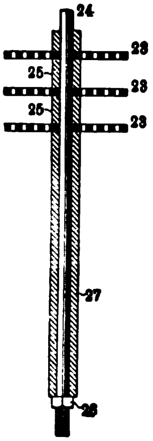
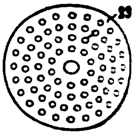


Fig. 454.



controlled, the heat being supplied from the gas-burner 18 and the annular burners 17 and 19. The mica-covered peep-holes, 22, enable observations to be made of the colour attained within, which should be a dull red opposite the upper portion of the contact-material. Directions are given for regulating the temperature as indicated at 10, 14, and 37. In the contact-material holder, the rod 24, removable from the top on withdrawing the cover 8, has strung upon it a series of perforated iron plates, 23 (figs. 453 and 454), distanced by sections of piping, 25, and the bottom plate is distanced from the nut 26 on the bottom of the rod by the section of piping 27; this latter section in charging the apparatus is dropped down the rod followed by a perforated plate, on to which is scattered a certain quantity of 10 per cent. platinized asbestos; one of the piping sections is then dropped into position and a perforated plate, and so on until the apparatus is charged. This apparatus is stated to have accomplished an average inversion of 95·9 per cent. while making sulphuric anhydride at a stated rate, the gases used containing 11·5 per cent. SO_2.

The B. P. No. 10,729, 23rd May, 1901, of the Badische A. & S. Fabrik prescribes the use of the oxides of iron, copper, or chromium as substrata for platinum black, to be produced per example, as follows:—145 parts of burnt pyrites, entirely free from arsenic (this is essential) in pieces about the size of a pea, screened so as to be free from dust, are impregnated with 30 parts of a solution of platinum chloride containing 17 grams platinum to the litre. The resulting product can be used at once as a catalyzer, or may first be heated. Such bodies are not molecular mixtures like those obtained by means of organic fabrics (comp. Porter's patent, *infrà*), but are formed of granules of metallic oxides covered with a layer of platinum. The catalytic action of the platinum is supported or increased by that of the oxides, and the product acts at least as well as platinized asbestos. These contact-bodies are cheap, offer great resistance to heat and chemical action, and require no special arrangements for preventing the pressure on the contact-material from forming an impermeable mass.

The annual production of sulphuric anhydride at the Ludwigshafen works of the Badische is stated by Knietsch:—

In 1888 = 18,500 tons.
„ 1894 = 39,000 „
„ 1899 = 89,600 „
„ 1900 = 116,000 „

The following communication, made to me directly, by the Badische Anilin- und Sodafabrik, is here given verbatim as transmitted to me by the firm.

Contribution to Lunge's Text-book, 3rd Ed.

In a lecture delivered before the German Chemical Society (*cf.* Berichte, 1901, vol. xxxiv. p. 4079), R. Knietsch has already made detailed communications as to inventions of the Badische Anilin- und Sodafabrik in the field of the manufacture of sulphuric acid by the contact-process, and as to the position which must be attributed to these inventions in the general history of the contact-process. The following additional facts are supplied at the desire of the author of this book by way of supplement to the publication mentioned.

We originally procured the fuming sulphuric acid that we required for the production of our colouring-matters from J. D. Starck in Bohemia, as did also all other colour factories. In the year 1875, Winkler published his epoch-making proposal to use the mixture of SO_2 and O in their combining proportions, as obtained by the decomposition of ordinary concentrated sulphuric acid at a red-heat and removal of the aqueous vapour, in the manufacture of fuming sulphuric acid according to the contact-process by passing the mixed gases over platinized contact-substances. We at once adopted this process, but there were such considerable difficulties in effecting the process on the manufacturing scale that we proceeded to experiment with burner-gases. These experiments were begun in the year 1881, as we can see from our records, and were carried on uninterruptedly, although for a time we were licensed to use the process of Schröder and Hänisch, which starts from gas containing approximately one hundred per cent. of sulphur dioxide. This process was tried, but subsequently dropped.

The introduction of the use of burner-gases in the contact-process required the solution of a series of further preliminary problems, and the very unfavourable results which were at first obtained were really such as to leave but little hope of any success when using burner-gases, and the idea of replacing the lead-chamber process by the contact-process was apparently altogether out of the question. At that time it would have been regarded as highly satisfactory if it had been possible when using burner-gases to replace the complicated and expensive Winkler process for producing fuming sulphuric acid by a simpler and cheaper process. The turning point in our experimental work was only reached when R. Knietsch in our laboratory made the pioneer inventions, which are described in the lecture already referred to (comp. *supra* p. 1012). These were based upon entirely new observations and experimental results.

As stated in the lecture, there are inventions with reference to all the stages of the contact-process, especially with reference to the preliminary treatment of the gases (absolute purification from deleterious ingredients), the actual contact-process (cooling the contact-mass and working without pressure and apparatus for these purposes), and to the absorption. The technical success of these inventions entirely surpasses anything that was deemed possible from the state of the art at that time, as shown by the literature of the subject and by the results obtained in practice. These inventions have resulted in the possibility not merely of producing fuming or ordinary concentrated sulphuric acid far cheaper than was formerly the case, but, further, it is possible to substitute with advantage the contact-process for the lead-chamber process in the manufacture of ordinary chamber-acid.

It is sufficient for us to refer to the report of the lecture in the 'Berichte' for the details of the invention, and in this report the literature of the subject and the views that were taken by technical men are summarized *. By way of supplement to the literature there noticed, we will here only mention that all that was known of the process carried out at Freiberg previous to the lecture of Winkler in Hanover in 1900 (*cf.* Zeitschrift für angew. Chemie, 1900, p. 731) is the communication of Schnabel in his 'Text-book of General Metallurgy,' 1st edition, 1890, p. 516. The passage runs as follows:—

"The fumes from the calcining-furnaces, which can be used for the manufacture of sulphuric acid, can also be employed for the production of sulphuric anhydride. This is effected at Freiberg with a small proportion of the roaster-gases. These are at first dried by passing them up towers whilst a spray of concentrated sulphuric acid descends in the opposite direction, then the gases enter closed heated vessels containing the platinized asbestos. Here, in consequence of the catalytic action, sulphuric anhydride is formed from the sulphurous acid and oxygen. The fumes containing the anhydride then enter a tower in which concentrated sulphuric acid drips down and absorbs the anhydride, and the anhydride is distilled off from the liquid so obtained. The gases leaving the absorption-towers still contain sulphurous acid. This is passed into the lead chambers together with the other burner-gases intended for the manufacture of sulphuric acid. The earlier experiments on the conversion of sulphurous acid from the calcining-furnaces into sulphuric acid by catalytic action had a negative result until Winkler introduced the process described." *

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* It is, however, unfortunately the fact that, even in text-books published since the lecture, mistaken descriptions are given of the fundamental principles and the nature of our inventions. (See, for instance, the latest edition of the 'Text-book of Chemical Technology' by Ferdinand Fischer, publishedin 1903.)

By the introduction of our invention into our factory on the large scale, we have been in a position since the early nineties to outdo our competitors in the home market, not only with fuming, but also with concentrated sulphuric acid. But the attainment of the great object which we deliberately aimed at, namely, to improve the new process so that even for the manufacture of ordinary dilute sulphuric acid it should become superior to the lead-chamber process, required still further energetic work.

During this period of the development an event occurred which threatened to deprive us of a great part of the fruits of the labours which we had been carrying out with such great pains for many years, and, to a certain extent, we must admit that we have suffered loss. Our first intimation as to the matter referred to came from various factories that supply us with our apparatus. They informed us that a Dutch factory for the manufacture of

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* We take this opportunity of remarking that this passage reappears in similar form in the 2nd edition of Schnabel's Text-book just issued, 1903, p. 584. There is the further information that when using this process only about half of the sulphurous acid contained in the gases was converted into anhydride. After this, the advances secured by our process are discussed, p. 585 (compare a careful purification of the roaster-gases from all admixtures which are deleterious in the process and a suitable arrangement of the contact-apparatus). It is true that our name and our patents are not mentioned, and there is the further remark that the production of chamber-acid by the contact-process is dearer than by the chamber-process, but the additional explanations that we give will show this statement is not true in the general form in which it is made.

sulphuric acid had ordered apparatus for the manufacture according to the catalytic process, and the drawings sent in showed that part of the apparatus required was identical, and part agreed in essential points, with the peculiar sulphuric-acid apparatus that existed solely in our factory. There could be no doubt that there had been a betrayal of our factory secrets, and we immediately suspected a mechanic, Carl Daub, who had been engaged in mounting the plant of a new sulphuric-acid factory, and had been dismissed from the works towards the end of 1895. This suspicion has proved to be fully correct, for it was found that this workman whilst in our factory systematically spied out our sulphuric-acid process, which was treated as a strict secret, as far as he possibly could. He also made copies of drawings and the like. Together with his brother Friedrich Daub, who was engaged as a chemist in the Dutch factory referred to, and who assisted him in formulating the questions to be put to the workmen in the sulphuric-acid department, he endeavoured to make capital out of his illegitimate knowledge and immediately after leaving us he entered the Dutch factory. After this Friedrich Daub sent offers to all important sulphuric-acid factories here and abroad, offering "his" process for sale and explaining that it was identical with that carried out by us. Later on he advertised quite openly in the trade papers. Although the circumstances and, in part, the nature of the communication offered could leave little doubt, in the minds of all concerned in the matter, that this was a case of betrayal of factory secrets, nevertheless several factories entered into negotiations and received in the correspondence that followed, or in the verbal negotiations, the assurance that Carl Daub had been engaged in our factory for several years and had a "most thorough" knowledge of our apparatus, and that "although the drawings had perhaps not been obtained in the most respectable ('nobel') manner, still it was not to be feared that the Badische Anilin- and Sodafabrik could take any steps." In this connection drawings which agreed more or less with our arrangements were laid before the would-be customers under the condition of secrecy.

It is hardly within the scope of this communication to mention the steps that were taken against the brothers Daub, and with reference to the firms who were in negotiation with them. We will only mention that amongst other things we sent a circular to all interested parties, and in this way, in a number of cases, the negotiations that had been begun were broken off, whilst, on the other hand, a few firms, amongst them the Dutch firm mentioned and other sulphuric-acid factories abroad, entered into agreements with the brothers Daub and were not ashamed to acknowledge this.

Fortunately, the information as to our process which the Daubs had obtained by spying was imperfect, and in part false, probably especially owing to the dismissal of Daub before he had fully ascertained our secrets, and owing to the fact that his intention to carry on further correspondence with our workmen was frustrated. Still, the practical success of our inventions, as also, for instance, the existence of contact-stoves which work automatically and of our effective purification-plant for burner-gases, became known through the treachery of Daub. The certainty that there was a process of such efficiency that it was possible to replace the chamber-process was alone sufficient to excite a large number of persons to the endeavour to obtain for themselves a share in the new achievements. Ideas and plans which had been partly or entirely abandoned, as no practical success could be hoped from them, were immediately reconsidered after it became known that such success was really possible, and from that time on a flood of patent applications set in in all countries. It was therefore obviously desirable in our interest to draft immediately an account of our work and publish it in the form of patents; but after we had published the fundamental inventions in this way, and after the greatest difficulties had been overcome, those inventions had the look of being very simple and clear, and the phenomenon recurred which has been observed in the case of so many epoch-making inventions, namely, that others who had worked with less success now saw clearly the essentials for success. The causes of failure of their own experiments and the reasons for our successes and our process itself now appeared quite a "matter of course," and this the more readily, because it is a fact that many ideas of similar nature had from time to time been under consideration, although indeed, on account of the apparent hopelessness of the problem, they had not been worked out in detail. As a consequence, in the oppositions that were raised against the grant of our patents, the statement was made again and again that the processes described and the observations and experiments on which they were based were not new, and even where processes had to be acknowledged as novel, still in some cases they were described as "almost obvious and a matter of course." This is absolutely unjustified, as is already obvious from the universally acknowledged pre-eminent success achieved by our processes, which has been characterized by Clemens Winkler as "weltbewegend"—an expression difficult to translate, but which implies the creation of a sensation throughout the world (see 'Zeitschrift für angewandte Chemie,' 1900, p. 737).

We will in the first place deal with the perfect purification of technical gas-mixtures containing sulphurous acid (especially burner-gases) up to a point defined by us at which an optical and chemical test is satisfied (German Patent, 113,933; English Letters Patent, No. 15,948, 1898; American Patent, 687,770). It appears on the face of these patents that before our invention not even the necessity for the absolute purity of the gases in the defined sense was recognized, and further, of course, no means were known for carrying the purification to such a high degree. The necessity for such purity, and the means to be adopted for achieving it, could not be known, because it was first necessary that the deleterious action of some of the admixed impurities should be recognized, and some of these impurities, such as small quantities of sulphur or sulphuric-acid mist, owing to their nature, and, further, traces of arsenic, on account of its volatility at the temperature of the contact-process, could not be regarded as in any way dangerous. Before the specific poisons for the platinum contact-apparatus, in particular arsenic, had been discovered, and the fact that sulphur and sulphuric-acid mist served as carriers for these contact-substance poisons, and acted in just as deleterious a manner on the contact-mass, there was absolutely no reason to consider means for fully removing these substances, and these considerations had greater force because it was generally believed that when working with technical burner-gases from pyrites it was in the nature of things impossible to achieve a quantitative conversion of the sulphurous acid into SO_3.

But even after the necessity for this absolute purification from deleterious ingredients had been recognized, a great step was necessary before a serviceable process for this operation could be discovered. When, therefore, the necessity for this perfect purification of the gases and means for effecting the operation were subsequently declared by third parties to be known or almost obvious, it must be borne in mind that prior to our invention the purification of burner-gases had in no case been carried further than the removal of coarse impurities (the greater quantity of the flue-dust), whilst the complete removal of flue-dust and of the admixtures in the contact-gases which at high temperatures exist in the form of vapours, mist, or gases had not been achieved in cases where it had been attempted at all, and in the opinion of the highest authorities on this art (Lunge, Winkler, Schnabel) was regarded as absolutely impossible *.

We have been confronted with the process for the production of pure sulphurous acid from burner-gases of the German Patent, No. 26,181 (Hänisch and Schröder); but this has nothing in common with our process for purifying the burner-gases, for, quite apart from the complicated and expensive method of absorbing the sulphurous oxide in water and then expelling it again by boiling, this process does not on the one hand in any way involve the same fundamental intention as ours—namely, to remove from the burner-gases just those substances which are deleterious, which, however, at that time were not even known to be deleterious. Again, according to this process, which had for its end the production of pure sulphurous acid for other purposes, concentrated sulphurous acid containing nearly one hundred per cent. SO_2 is obtained, and in order to make this applicable for the contact-process this has to be mixed with oxygen or air, whilst according to our process, apart from the deliberately purposed removal of all deleterious impurities, they are not changed in their composition, but contain SO_2, O, and N in the same proportions.

We will now deal with another constantly recurring objection,

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* Immediately before our application for a patent for this process was filed, there was one in full accordance with this view (patent No. 102,204, 17th May, 1898, of the Aktien-Gesellschaft für Zinc Industrie, vorm. Grillo in Oberhausen, and Dr. Max Schroeder, Düsseldorf). The application referred to the production of contact-bodies that could be readily regenerated, and as the reason for the invention the statement is made that "the burner-gases always contain some flue-dust, even after careful purification, and consequently, in course of time, the contact-bodies become covered with a layer of almost impervious matter, and this diminishes their effect." The applicants for this patent had, however, in no way apprehended the existence of the specific poisons for contact-substances, such as arsenic, which were discovered by us, and, even after our inventions were published, the firm named directly contended that arsenic was not injurious to the contact-mass. (Comp. Journ. Soc. Chem. Ind. 1903, p. 350.

viz. the fact that it had already been observed that arsenic has a deleterious action on platinum sponge as used in the Döbereiner igniting-apparatus. Those who wished to regard this as affecting in any way the novelty of our process ignored the fact that this little apparatus not only deals with quite a different chemical process from that under consideration, but also that in this igniter the platinum has to become heated from the temperature of the air to the temperature at which hydrogen ignites, whilst the requirements in respect to temperature in the contact-process in the manufacture of sulphuric acid are altogether different. Analogy cannot be relied upon in this field of work; for instance, palladium, which belongs to the same group of elements as platinum, behaves towards hydrogen in a similar manner to it, while it is practically altogether inapplicable for the union of SO_2 and O.

We can state with satisfaction that the German Imperial Patent Office accepted our arguments as to the novelty of our process and the observations upon which it is based, and granted us the patent for the purification process without any limitations, as applied for by us, rejecting the oppositions in both instances.

In view of the fact that the means devised by us for effecting the purification were new, and based on the discovery of new fundamental principles, it is a matter of course that other and similar means of achieving the purification should fall within the scope of our patents. Our process, for instance, can be carried out in such a way that the intimate contact of the gases and the washing-liquid is brought about, instead of by washing, as we had done, by the essentially identical process of wet filtering. We have already used this process with complete success for the process in question (*cf.* 'Berichte,' xxxiv. p. 4081).

It has also been urged against our cooling-process (German Patent, No. 113,932; English Letters Patent, No. 15,497 and No. 15,949 of 1898; American patents, Nos. 652,119, 1900, 688,020, 1901, 688,469/72, 1901, 690,062, 1901, and 692,018, 1902), in the oppositions that were raised against the grant in Germany, that it was destitute of novelty and almost obvious.

The novelty and originality of the cooling-process can be seen at once from the state of the art as shown in the literature at that time. It appears from the literature that it was known that the contact-process could only be effected at an elevated temperature, and that it was consequently necessary to heat the apparatus, and, with reference to the temperature of the contact-substance, the only point to which attention had been called was economy of fuel. For this purpose endeavours were made to avoid a special heating of the contact-apparatus by surrounding it with heated gases whose heat would otherwise have been lost. Or, again, the gases entering upon the reaction were permitted to enter the contact-apparatus at a sufficiently high temperature to make a further heating unnecessary (*cf.* 2nd edition of this Text-book, vol. iii. p. 815). In this connection it must be borne in mind that the apparatus described in that place * was intended for working up gases containing about 25 per cent. of SO_2, and not for burner-gases, so that the heat of reaction developed in this case would have caused a far higher rise of temperature than that which occurs when ordinary burner-gases containing from 6 to 8 per cent. by volume of SO_2 are used. Even though it is to be regarded as known that the temperature of the contact-apparatus should not rise "altogether too high," nevertheless there is no known mention anywhere in literature of a cooling-operation, far less of any deliberate and intended cooling of the apparatus. The universal belief was that if the percentage of conversion decreased, partly owing to the action of the contact-poisons, which were then unknown, or partly in consequence of the heat of reaction causing the deleterious overheating of the contact-mass, which was also unknown, then the reason was that the ultimate capacity of the contact-mass had been reached, and that therefore if the same percentage conversion was required, the current of gas must be made slower. So long as the work was conducted on these principles, namely, that of heating the contact-apparatus, or at least preventing cooling as far as possible, it is obvious that the quantity of gas that could be treated, and consequently the efficiency of the apparatus, must be relatively very limited, as can now, after the publication of our process, be readily understood by everyone skilled in the manufacture.

The apparatus described in the English Patent, No. 3166 of 1888 (Ellice-Clark), also employs the principle above mentioned of heating the contact-apparatus, and in this case the heating was effected by the waste heat of the pyrites-burners. In this patent, which is only mentioned casually in the second edition of this book, the inventor, George Lunge, directs that "the temperature in that part of the apparatus where the union of SO_2 and O takes place must be carefully regulated, and not be too high or too low, preferably at or under a dark red-heat." This corresponds simply to that which was known up to that time in this respect (*cf.* Squire's English Patent, No. 3278 of 1875). The contact-tubes, even though their temperature is to be regulated, are in this case, just as in every previous case, heated by the heat of the pyrites-burners, and not in any way cooled. In this patent also there is no suggestion whatever that a special temperature favourable for the contact-process shall be brought about by cooling.

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* We should like to state that up to the present day we know of no factory in which this apparatus was ever in practical use.

We have shown that our process, based upon the principle of cooling, is a completely new one, and opens up a course that was previously entirely unknown; but the great technical advance that is secured by the invention of the German patent No. 113,932 (English Patents, Nos. 15,497 and 15,949 of 1896; Amer. Patents, Nos. 652,119, 1900, 688,020, 1901, 688,469/72, 1901, 690,062, 1901, and 692,018, 1902) results from the fact that in place of a crude empirical method of working based upon a diminution of the efficiency of the apparatus, a quite new inventive idea and a method of working of the greatest importance are adopted, whereby the work is rationally conducted and the well-understood effects are deliberately caused. This new method of working is the regulated external cooling of the contact-apparatus; by this means the heat of reaction, which is the cause of the deleterious overheating of the apparatus and consequent dissociation of SO_3, is removed, with the result that the same quantity of contact-substance can now deal with a considerably larger quantity of gas, and the efficiency of the apparatus is raised to the highest possible degree. There is the further technical advantage that the cooling can be effected by the reaction-gases themselves, so that these need not be preliminarily heated for the subsequent conversion.

It can be seen from this that in our cooling-process the heat of reaction can simultaneously be used; but it should be observed that the method of working in using the heat of reaction, as can be seen from what has been said without further explanation, differs entirely in principle from that described in the German patent No. 105,876 (English Letters Patent, No. 6057 of 1898), in which the heat contained in the reaction-gases which have already left the contact-stove is used, whilst the removal of the excess heat of reaction during the reaction, and consequently the increase in the efficiency of the apparatus, cannot possibly be effected.

By the use of our cooling-process, not only is the achievement of a higher degree of conversion of SO_2 into SO_3 (96 to 98 per cent.) secured than has hitherto been effected, but also, and this is just as important, simultaneously the efficiency of the contact-mass is used up to its utmost limit.

But it is not to be thought that this effect is in any way achieved by maintaining a definite uniform temperature in all parts of the contact-apparatus. In none of our patents do we prescribe the use of a definite uniform temperature; on the contrary, in the examples we quote we only mention the temperature of the gas entering and of that leaving the apparatus. In view of the nature of the contact-process and the cooling-process, especially when the cooling is effected by a counter current, it is impossible to maintain a uniform temperature throughout the contact-apparatus. If the advantages of our cooling-process with respect to the efficiency of the contact-mass are to be fully enjoyed, an exceedingly vigorous reaction will take place in the first layers of the contact-mass, in consequence of the great burden that is thrown upon them, and consequently at these first layers there is a rapid rise of temperature. By the external cooling the heat is gradually removed as the gases pass on, and so the temperature is again brought to the stage at which the most perfect conversion takes place (see also the curve showing the velocity of the reaction in the 'Berichte,' 1901, p. 4098). The temperature in the interior of the contact-chamber, as employed in manufacturing on the large scale, rises rapidly to a maximum, which occurs when the gases have passed through approximately one quarter of the contact-mass. From this maximum it gradually falls to about 380° or 450° C., between which temperatures the conversion of from 96 to 98 per cent. is possible. It is wrong, therefore, to imagine that our cooling-process proceeds as a matter of fact at any definite temperature or between narrowly limited temperatures, and the most favourable conditions of temperature must be determined for each single case. Direct observations upon apparatus that have been in use for many years past in the factory have shown that the temperature is exactly as above described in the contact-mass, and that the temperature at which the gases enter, the maximum temperature, and the final temperature may be varied within wide limits without essential alteration of the quantitative result.

If, therefore, the temperature of the various parts of the contact-space be so arranged that at first there is a low temperature, later on a more or less elevated temperature, then again a lower temperature, or, indeed, if the first phase be nominally dropped so that at first the operation is conducted at a high temperature and then at a lower temperature, these variations are nothing more or less than the actual cooling-process patented by us in the German patent No. 113,932. Of course, modifications can be made in the arrangement of the contact-mass in the tubes; for instance, the contact-mass can be arranged outside horizontal cooling-tubes through which the cooling-gases pass. In every such case the process of cooling described in our patent is used, and must, indeed, be used if the practical quantitative conversion of SO_2 into SO_3 and simultaneously the maximum efficiency of the contact-mass is actually to be achieved, for there is no other means of attaining this result.

The same is the case when apparatus in the form of pots or large vessels are used, if these are to be so worked as to yield what is today regarded as a sufficient conversion. Such apparatus, even after it is furnished with non-conducting covering, nevertheless gives off heat, that is to say, some cooling takes place. This can at once be seen in such cases where the temperature, exactly as in our process, rises at first and subsequently falls as the gases pass through the apparatus; but the cooling in these cases cannot be regulated but remains constant, so that such apparatus suffers from the disadvantage that only a certain amount of heat can be got rid of, so that each apparatus can only work with a definite quantity of gas, which must be empirically ascertained for the apparatus. As against such apparatus, the special forms described in our German patent No. 113,932 have the essential advantage that they are, within wide limits, independent of the quantity and concentration of the gases. At the same time, our apparatus when it has once been regulated for definite conditions works automatically within certain limits, so that the means for regulating need only be used again when the quantity or the concentration of the gas changes considerably. A further special characteristic of our process is that it works without pressure, and in this way the idea formerly held, namely, that a high yield of sulphuric anhydride could only be obtained by employing pressure, has been demonstrated to be false with certainty. It is true that, theoretically, the equilibrium of the action would be changed favourably for the formation of SO_3 by the application of pressure; but already, at a time when the various theories of physical chemistry were but little developed, we proved experimentally that under the conditions of technical manufacture according to the contact-process it is possible without pressure to arrive at a practically quantitative yield, and that therefore the matter of pressure is not only of no great value, but is of such slight importance that it can be absolutely neglected. Similarly the belief was held, based upon the law of action of mass, that a dilution of the gases with air had a deleterious influence, and this view was expressed by many. In this case also we proved the right way by experiment before the development of physical chemistry.

Our recognition that pressure was of no practical importance, and that an admixture of the gas with air had no harmful influence, was of the greatest economic value for the contact-process, for after this it was clearly seen that ordinary dilute burner-gases could be employed and means could be devised for passing the gases through the contact-mass whilst opposing as little resistance as possible, so that the mechanical force required for moving the gases could be reduced to a minimum.

The recognition that pressure has no essential influence is the basis upon which the apparatus of our German patent No. 119,059, and the process of our patent No. 133,713, is based (English Letters Patent, No. 15,950 of 1898). The subject matter of these patents, as also of those referring to our absorption process, are discussed in the 'Berichte' at the place already cited.

We will finally mention the only process in which another contact-material, namely, burnt pyrites, is used. The inventors of this process believed at first that they could by its use complete the reaction, but, nevertheless, they subsequently found that in a contact-stove containing iron oxide only 60 per cent. of the gases was converted in one operation, the remainder after being completely freed from the catalytic poisons discovered by us has then to be combined with the aid of platinum.

In the lecture reported in the 'Berichte,' to which we have several times referred, the importance of our process was illustrated by mentioning the quantity of SO_3 produced annually by our process (*suprà*, p. 1025); since that time the production in our factory, as also in particular the production of our licenses, is essentially greater and now amounts to about 200,000 tons of sulphuric anhydride annually. This quantity is continually increasing.

II. *Process of the Farbwerke, vormals Meister, Lucius, & Brüning, at Höchst.*

This process has been worked out by Dr. C. Krauss and is described below by himself. Patents: B. P. No. 6057, March 11, 1898; No. 14,728, July 4, 1898; No. 285, Jan. 5, 1899; No. 1385, Jan. 21, 1901; No. 2368, Feb. 4, 1901; No. 3161, Feb. 7, 1902; No. 4026, Feb. 17, 1902. U.S. P. (Krauss and von Berneck) No. 700,512, May 20, 1902. G. P. No. 135,887, Feb. 7, 1902.

The following communication has been made to me by the above firm. It is penned by Dr. C. Krauss, the real inventor of the processes in question, and Dr. Rudolph Müller von Berneck:—

The Höchst Farbwerke, one of the first firms which have made sulphuric anhydride on a large scale by the contact-process, at first proceeded, according to Winkler, by decomposing concentrated sulphuric acid at a high temperature into SO_2, O_2, and H_2O, removing the latter and passing the SO_2+O_2 over platinum asbestos. Attempts were made many years ago to convert purified pyrites-kiln gases into SO_3, but not with technically satisfactory success. Therefore extended experiments were made, both on a large scale and in the laboratory, with pure liquid sulphur dioxide and dry air, afterwards with gases produced by burning sulphur in air, which led to the result that a satisfactory yield of SO_3 from SO_2 was easily attained by keeping the reaction within definite limits of temperature. George Lunge has the merit of having first made this observation and having first publicly expressed it. In his British patent, No. 3166, of 1888, taken for him by Ellice-Clark, he says, verbatim:—"The temperature in that part of the apparatus where the combination of SO_2 and O_2 takes place must be carefully regulated, and must be neither too high nor too low (preferably at or below a dull red-heat)." *

On the strength of their observations and trials, and on the strength of the fundamental discovery of Lunge, the Farbwerke erected a plant for making SO_3 from pyrites-kiln gases for a daily consumption of 15 tons pyrites. The gases were first freed from all impurities by washing with steam, water, and a solution of bisulphate (for the removal of fluorine and chlorine compounds), and drying by sulphuric monohydrate in specially constructed apparatus. They were then passed into the contact-furnace, fig. 455. Here they were heated in the pipes HH, and subjected

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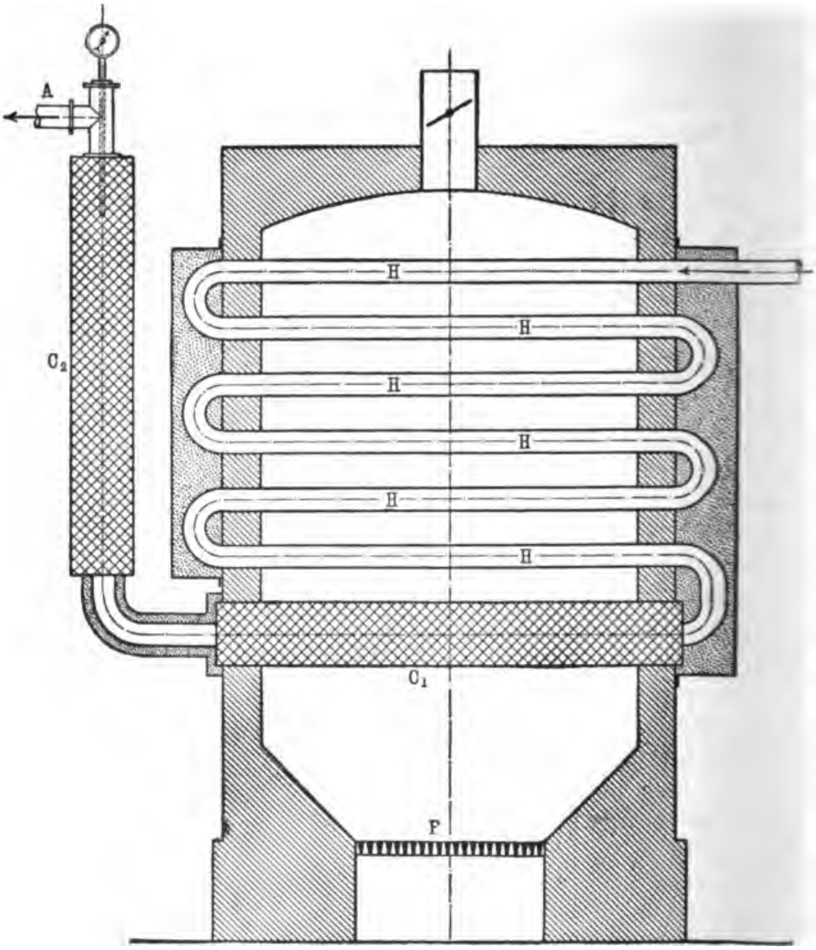
* I do not myself claim priority in this respect. Long before the above patent it had been pointed out that the temperature of the contact-oven must be regulated as above; comp. also *suprà*, p. 1035.—G. L.

Fig. 455.



to catalysis in the two contact-retorts C_1 and C_2. Retort C_1 was placed within the furnace above the fire-grate F, retort C_2 outside the furnace. The gaseous current and the fire were regulated in such manner that the gases issuing from retort C_2 at A showed a temperature of 400°–450° C. The gases were then cooled, and the SO_3 absorbed by concentrated sulphuric acid in cast-iron absorbers placed terrace-wise, so that ordinary acid was run in at the top, and fuming acid run off at the bottom. The gases were compelled to bubble through the acid in each absorber; these were cooled from the outside by flowing water.

This plant worked satisfactorily for many years; but soon the idea arose of gaining the considerable amount of heat required for heating the gases from one of the sources of heat offered by the process itself. As the most convenient of these was chosen the heat stored up in the gases issuing after the reaction from the the contact-retorts. The exchange of heat was brought about by the apparatus shown in fig. 456, containing both the heat-exchange and the contact-space. The purified pyrites-kiln gases enter at E, play round the pipes R, whereby they are heated to 400° C., and at the top enter into the catalyzer C. The SO_3 gases formed descend in the pipes R, where they yield up their heat to the SO_2 gases, and leave the apparatus at A.

Figs. 457 and 458 show different forms of apparatus for this purpose.

The result of this work was the G. P. 105,876 and B. P. 6057 of 1898, in which is claimed "the method of raising the gases to the temperature required for the reaction, by transferring to them heat from the produced sulphur trioxide." The transference is effected by a simple counter-current apparatus.

The working out of this process on the large scale commenced with great difficulties. Chiefly in consequence of the large dimensions of the apparatus, it was not easy to keep the temperature within the limits most favourable for the production of SO_3. This was remedied by G. P. 119,505 (B. P. 285, of 1899). Here the temperature of the contact-space is regulated by mixing the reaction-gases overheated therein with cold SO_2 gases, and thereby lowering the temperature for the time being.

In connection with the above work, investigations were made respecting the influence of the compression of roasting-gases on the formation of SO_3. Schroeder and Haenisch (G. P. 42,215) had

Fig. 456.

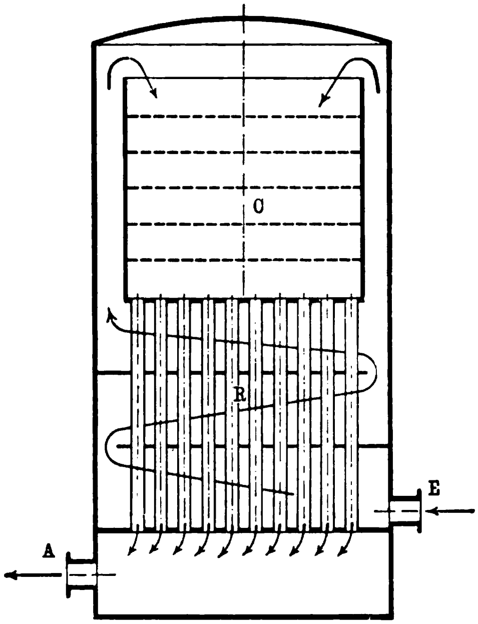


Fig. 457.

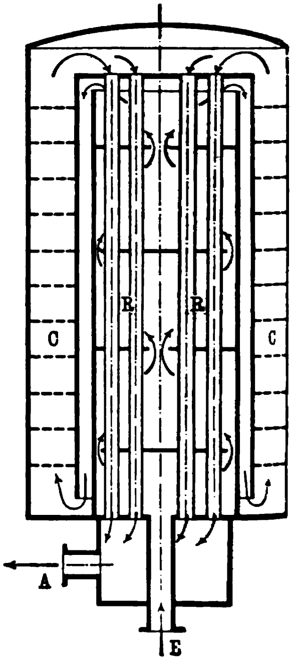
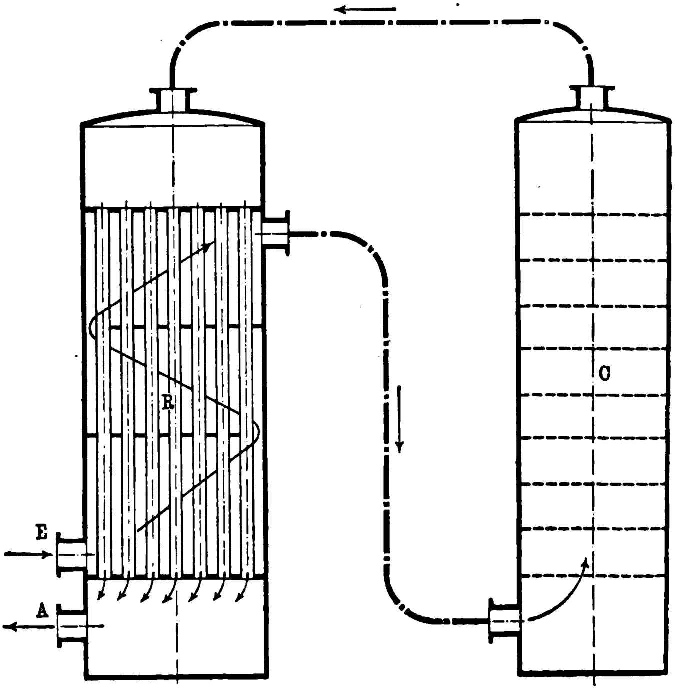


Fig. 458.



proposed to work at a pressure of 2 or 3 atmospheres above the ordinary pressure. Our investigations showed, as is distinctly stated in the first of the above-mentioned patents, that "the reaction goes on at any pressure, but best quantitatively at a plus-pressure." But they further showed that the advantage produced by artificial high pressure in slightly altering the chemical equilibrium in favour of the formation of SO_3 is not at all equivalent to the increased consumption of steam required for that high pressure. Our efforts were therefore from the first directed towards reducing the inner resistance of the apparatus, in order to reduce the expenses for steam.

Pressure certainly plays an important part in the reaction, as is proved by theoretical reasoning instituted by Professor Bredig, with the result that under certain circumstances pressure exercises a considerable effect on the equilibrium $(2SO_2+O_2)+x \rightleftarrows 2SO_3$; but with the pressures possible in technical operations that influence is very slight, and the advantage gained thereby does not correspond to the increased expense for motive-power.

A knowledge of the equilibrium-constants was very valuable, as presenting a security for attaining the equilibrium as soon as the constant calculated from the analytical data shows the proper value for the temperature in question. If the constants are known for one or several temperatures, the value of K can be calculated for any other temperature by means of the reaction-heat.

The constants were determined as follows:—Tubes of Jena high-pressure glass holding 20 c.c. were drawn out into capillaries at both ends, and charged with about 5 grams SO_3. One of the capillaries was sealed, and the air pumped out as well as possible. This is more easily performed if the SO_3 is heated to boiling, its heavy vapours driving out the air. When about nine-tenths of the SO_3 had been evaporated, the second capillary was sealed as well. The tubes, which contained about 1 metre of platinum wire as a catalyzer, were heated during 3 or 4 days in a thermostat to the required temperature. Without platinum wire the reaction was so slow that the equilibrium was not reached even after heating for weeks.

The temperatures ranged between 465° and 515° C. At lower temperatures the velocity of reaction was too small, at higher temperatures the glass became soft and the tubes were blown out. After the equilibrium was attained, the contents of the tubes were analyzed, and the constants calculated therefrom. This requires knowing the concentrations of SO_3, SO_2, and O; but as it is very difficult to estimate all three, only SO_3 and SO_2 were estimated; the concentration of SO_2 must be proportional to that of O_2. The formula

$$\frac{(C \,.\, SO_3)^2}{(C \,.\, SO_2)^2 + C \,.\, O_2} = K$$

must then be changed into

$$\frac{(C \,.\, SO_3)^2}{(C \,.\, SO_2)^2} = K.$$

This formula was applied to the calculation of the constants. The single values thus found did not agree very well, because the dust absorbed some oxygen, and the glass tubes are to some extent acted upon ; in a few cases even the platinum wire showed some action by a bluish-black colour, which vanished when igniting the wire in the air, and therefore probably consisted of a platinum oxide.

The following average values for K were obtained from 14 (respectively 12) experiments :—

At 515° C.	At 465° C.
18,590,000	83,618,000.

The volume of the tubes was expressed in litres.

To check these values, other similar tubes were charged with a mixture of $2SO_2 + O_2$, and heated till the equilibrium was attained. The results agreed with those previously found in the order of magnitudes.

If we insert these equilibrium-constants in the formula expressing the proportion of reaction-heats to equilibrium-constants (Nernst, Theor. Chem. p. 599), we find the reaction-heat Q, if K_1 is the equilibrium-constant at T_1, K_2 the same at T_2:

$$Q = \frac{4 \cdot 584 \, (\log K_2 - \log K_1) \, T_1 T_2}{T_2 - T_1} \text{ calories,}$$

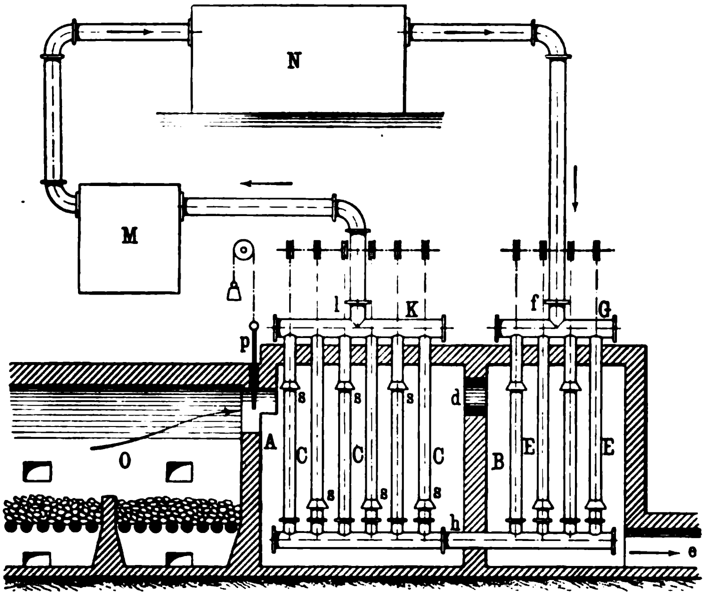
$$Q = \frac{4 \cdot 584 \, (\log 83{,}618{,}000 - \log 18{,}590{,}000) \, 787 \cdot 737}{50}$$

$$= 34{,}670 \text{ calories};$$

hence $(SO_2, O) = 17{\cdot}3$ calories, whereas Thomson gives 20·5 and Berthelot 22·6 calories (Ostwald, Lehrb. ii. 1, pp. 123, 124).

After, in the above-described way, the very considerable expense for the direct heating of the gases in the contact-process had been eliminated, and the cost of motive-power for high pressure had been reduced, efforts were made for saving as much as possible of the power for propelling the immense volume of gases through the apparatus. Chimney-draught appeared insufficient, on account of the considerable inner resistance, especially in the apparatus for purifying the gases and absorbing the SO_3. Hence steam had to be retained as the source of motive-power, and attempts were made to cheapen its production by utilizing the combustion-heat of pyrites. This was done in the way shown in fig. 459. The gases leave the pyrites-kiln O with a temperature of 600° or 700° C., and enter a chamber divided by a partition into two parts, A and B. In A they play round iron pipes C, provided with movable scrapers *s*, and yield up part of their heat to the water circulating therein, thereby producing some steam. They now pass through *d* into the second chamber B, and again play

Fig. 459.



round pipes E, provided with scrapers and connected with pipes C C. In E the gases yield up their remaining heat. The water travels in the opposite direction to the gases, entering at *f* and leaving the pipes at K in a heated state. The steam thus generated issues at *l*, passes into the heat-regulator M, and from there with as even a temperature as possible into the "cold-steam engine" N, from which the condensing water flows back to G. These experiments are not yet brought to a satisfactory issue.

In connection with these technical experiments, exhaustive laboratory researches were made on the catalytic process, which are still partially in progress.

Since in the reaction $2SO_2 + O_2 \rightleftarrows 2SO_3$ the concentration of two substances is changed, that reaction, according to our present views, ought to be of the second or third order. But since in technical kiln-gas, containing 6 or 7 volume per cent. SO_2, there is a very considerable excess of oxygen, practically only the concentration of SO_2 will alter to a considerable extent, and the process will go on approximately as a reaction of the first order, *i.e.* the quantity transformed in the unit of time will be directly proportionate to the concentration of SO_2.

If we denote by 1 the time required for transforming the first 10 per cent. SO_2 of that present in the kiln-gases into SO_3, during the time 2, from the residual gases, now containing only 90 per cent. of the original SO_2, not 10 per cent., but only 9 per cent. will be transformed. In order to catalyze the whole of the 10 per cent., we must employ 10/9 units of time, and so forth, so that we obtain the following series:—

Per cent. SO_2.	Units of Time = Units of Catalysis.	
100—90	10/10 = 1	14·3
90—80	10/9 = 1·11	
80—70	10/8 = 1·25	
70—60	10/7 = 1·43	
60—50	10/6 = 1·67	
50—40	10/5 = 2·00	
40—30	10/4 = 2·50	
30—20	10/3 = 3·33	
20—10	10/2 = 5	15
10—0	10/1 = 10	

When working with a continuous stream of gases, "time" means the time of contact with the catalyzer, and "unit of time" the unit of catalysis 1 required for transforming the first 10 per cent. SO_2. We then see that the first 80 per cent. SO_2 is transformed into SO_3 in about the same time or by the same quantity of catalyzer as is required for the transformation of the last 20 per cent. SO_2, assuming the temperatures to be equal.

In every chemical reaction, whether endothermic or exothermic, the velocity of reaction and the finally attained equilibrium depend on the temperature, or, in other words, under otherwise equal conditions, there belongs to each temperature a certain velocity of reaction and a certain equilibrium. We know that the velocity of reaction increases with the temperature, and thermodynamics teaches us that the equilibrium with the rise of temperature changes in that sense that those products increase which are formed with absorption of heat. Formerly nothing was found in literature concerning the temperature within the contact-space except the uncertain expression of "a red-heat." The above-mentioned British patent of Lunge's for the first time contains the demand that the temperature within the contact-space must be carefully regulated. This idea was taken up by the Höchst Farbwerke in their B. P. No. 285, 1899. But the aim of thorough rational work was not yet reached in that way, viz. to combine the largest possible velocity of reaction (the smallest possible amount of contact-substance) with the largest possible yield of SO_3. This was not easily attained in the manner previously followed. We may certainly increase at will the velocity of reaction by raising the temperature, but at the same time we change the equilibrium between SO_2, O_2, and SO_3. This is distinctly proved by experiment. At 408° the reaction was almost quantitative, at 500° only 90 per cent., at 530° only 80 per cent. of the SO_2 is transformed into SO_3.

A further result of the research was the surprising increase of the velocity of reaction with the rise of temperature. With finely divided platinum as a catalyzer, it is 60 or 80 times as great at 500° as at 400°, and increases still further at higher temperatures. We find that the same contact-mass which at 400° transforms 100 parts SO_2 into SO_3, at 520° transforms $80 \times 80 = 6400$ parts SO_2 into SO_3, and the proportion is still better at higher temperatures.

From these experimental results we conclude *that really great* *velocities of reaction, even when employing excellent catalyzers like finely-divided platinum, occur only at such temperatures at which the percentage yield of SO_3 begins to be inferior, and that a combination of both advantages is not possible so long as the whole contact-space is kept at a uniform temperature such as had hitherto been aimed at.*

Hence experiments were made for conducting the catalytic process within the contact-space at varying temperatures, viz. keeping the temperature in the first zone of reaction high enough for oxidizing most of the SO_2 into SO_3, and afterwards cooling down the gases to about 400°, at which temperature they pass through the second contact-zone, where the remainder of the SO_2 is oxidized. This is embodied in the B. P. No. 1385, 1901 (reprinted Chem. Tr. Journ. 1901, ii. p. 559).

Technically we can achieve that object, first, by placing before the present contact-chamber another smaller one, into which the reacting gases enter at a higher temperature, say 530°, and where 75–80 per cent. of the SO_2 is changed into SO_3. The gases are then cooled down to 400°, either from the outside by means of a tubular system or by mixing them with cold gases, which do not disturb the process, and are then passed through the second contact-space, where the remaining 20–25 per cent. SO_2 is almost entirely oxidized. A second, technically practicable way is this : to employ a very long contact-space, in which the gases enter at 530° and gradually cool down to about 430° before issuing.

As a matter of course the hotter contact-space will not be charged with platinum, but with cheaper contact-substances active at such high temperatures. For that purpose a great many substances were examined for their catalytic properties. The following were found to be active catalyzers :—

1. Platinum.
2. Vanadic, molybdic, and tungstic acid, also the complex compounds formed by these acids with each other.
3. The oxides and sulphates of iron, cobalt, nickel, copper, silver, manganese, chromium, uranium, &c.
4. The oxides of cerium, didymium, lanthanium, zirconium, thorium, titanium, silicon, and many rare elements.
5. Mixtures of the catalyzers with each other.

Among the metals of the platinum group only platinum itself comes into question. Iridium (against the ordinary notion) acts very slowly; so does palladium. Platinum under certain conditions is a good catalyzer already at 200° and is not approached in its action by any other known chemical substance.

Of the substances enumerated under No. 2, vanadic and tungstic acid act about equally well, molybdic acid less so. Of the group No. 3, the sulphates of nickel and cobalt are far the best and are superior even to vanadic acid. Iron acts only in the shape of peroxide. Ferrous compounds are first changed into ferric sulphate by absorbing SO_2 and O, and this quickly gives up SO_3, so that Fe_2O_3 remains behind as a catalyzer. Copper acts rather less than Ni and Co. Silver sulphate is a good catalyzer, uranium much less than the others, and gold not all.

The substances of class 4 are on the whole very slow catalyzers, but some, especially freshly precipitated silica, seem to increase the activity of certain catalyzers.

Much attention was also given to the so-called "contact-poisons." Very important observations were made in the laboratory and confirmed in practice. Of the substances examined, Hg and CO were found altogether innocuous. S and H_2O, the latter as steam or sulphuric-acid mist, impeded or stopped the reaction, according to the quantity of S or H_2O; but when these substances were removed from the gases, the contact worked as well as before. As, Se, Te, and Sb are strong contact-poisons, small quantities of which permanently disturb the activity of platinum; they seem to be oxidized to non-volatile oxides which combine with Pt. Besides these elements, another substance occurs in some kinds of pyrites which acts as a strong platinum poison, but which has not been identified up to the present. Especially selenium and tellurium cause a lasting poisoning. Antimony, thallium, and lead occur only in case of very imperfect purification. Arsenic is a momentary poison, but apparently disappears in course of time, especially when the gases contain traces of moisture. This is proved by the following fact:—If steam is mixed with the purified pyrites-kiln gases before entering the contact-space, the whole of the arsenic present in the latter is volatilized and the activity of the platinum is restored. Arsenic seems to act as a poison for nearly all other catalyzers as well *. This is the subject of a G. P. application, dated Feb. 5, 1902.

Further efforts were directed towards eliminating the platinum

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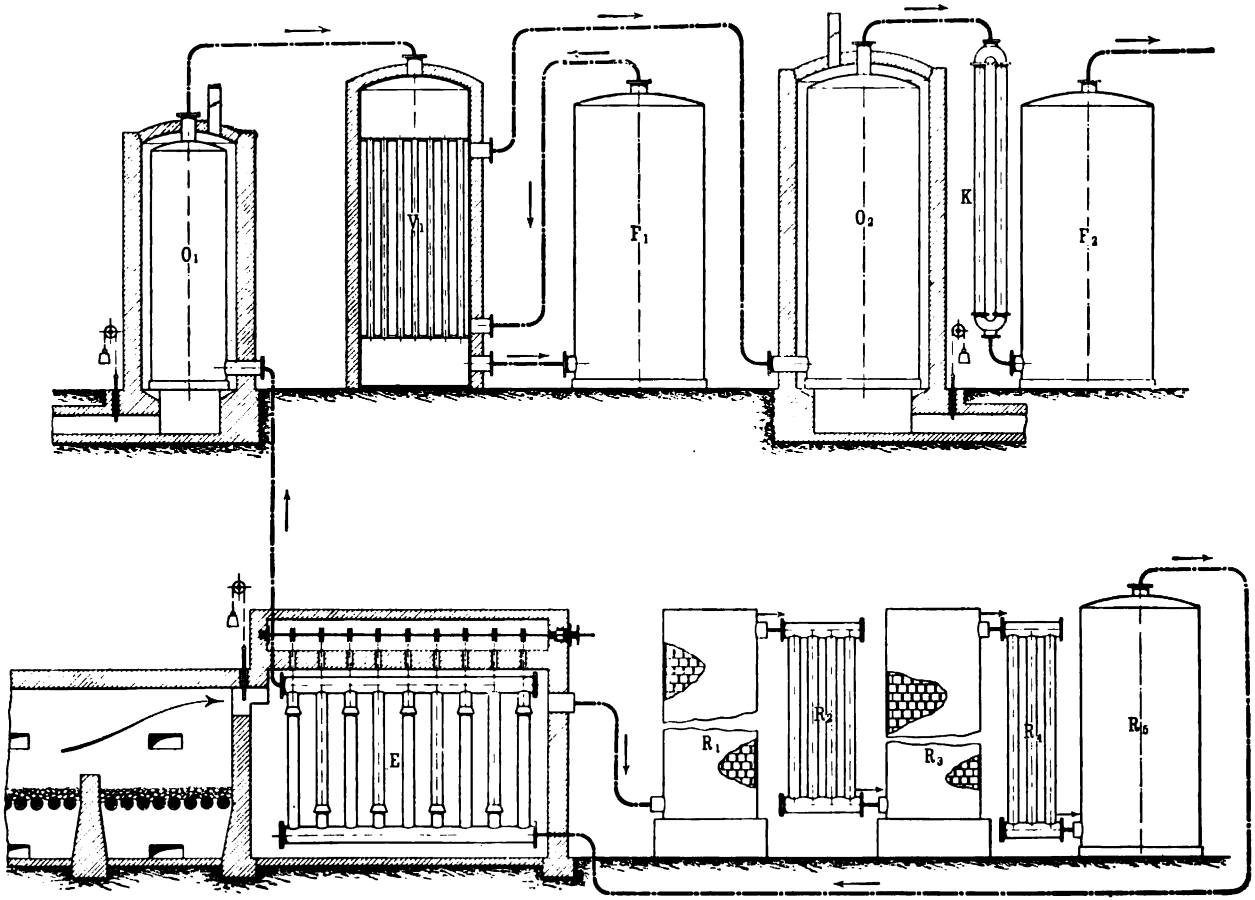
* Comp. p. 1008, as to the contrary.—G. L.

altogether. From the law of the action of masses it follows that, in order to convert at a certain temperature a maximum of SO_2 into SO_3, either the quantity of air should be greatly increased (which would be irrational on account of the expense of propelling the greatly increased mass of gases), *or the SO_3 formed should be removed from the gases and the latter catalized again.* This can be effected by cooling the gases after they have left the contact-space and have been partially converted into SO_3, removing the SO_3 by absorption, and passing the gases through a second contact-space. Suppose the temperature of the first contact-space to be 520°, and the contact-substance to be nickel sulphate. Here 80 per cent. of SO_2 is changed into SO_3. After removing the latter, 20 per cent. of the original SO_2 remains in the gases, which are now passed again over nickel sulphate at 520°; in this second case again about ⅘ of the 20 per cent. are changed in SO_3, or altogether 96 per cent., in lieu of the 80 per cent. possible at 520° with one contact-action. In the second contact it is not necessary to keep the temperature low enough for the most favourable equilibrium of SO_3, but here the very large increase of the velocity of reaction at higher temperatures may be utilized.

These facts are laid down in B. P. 2368, of 1901, and the work is then done in one of the following ways (1–4):—

1. (Fig. 460.) The pyrites-kiln gases issuing from the dust-chamber are cooled and purified in R_1, R_2, R_3, &c., and then passed through a series of pipes E, placed in the dust-chamber or otherwise, where they are heated by the hot burner-gas. These pipes are constructed to act as an economizer, with scrapers for removing any adhering flue-dust. The moving parts of the scrapers are placed in a closed box, or are protected by cup-joints or the like against the SO_2 gas present in the dust-chamber. The escape of these gases round the scrapers can also be prevented by slightly compressing the current before entering the chamber and thus producing a very slight minus-pressure therein.

The gases, preferably heated to 500° C. in E, now enter the contact-space O_1. Sometimes it is better to pass them first through an auxiliary heating-apparatus, to provide against any accidents, such as a cooling down of the kilns. In the oxidizer O_1 most of the SO_2 is converted into SO_3. The gases now pass into the heat-exchanger V_1, where they are cooled by yielding up their heat to the gases issuing in the opposite direction. The cooled gases are


O_1
V_1
F_1
O_2
K
F_2
E
R_1
R_2
R_3
R_4
R_5

deprived of their SO_3 in F_1, are then passed back into the heat-exchanger V_1, if necessary also through a special heat-regulator, and then into contact-space O_2, where most of the remaining SO_2 is transformed into SO_3. When issuing from O_2, the gases are cooled in K and the SO_3 is retained in F_2, either by strong sulphuric acid or by water or steam.

Of course these processes might be repeated over again, but this would not pay, as the second catalyzer already completes the conversion up to 95 per cent., which may be called technically quantitative.

2. The pyrites-kiln gases are cooled and purified in R_1, R_2, R_3, then heated up in the heat-exchanger V_1 and passed into the contact-space O_2, provided with heat-regulator, then passed back into V_1, where they yield up their heat. After taking out the SO_3 in F_2 the gases are heated in E, passed into O_1, and absorbed in F_1.

3. The purified gases are heated in the heat-exchanger V_1, passed through contact-space O_2, cooled in K, freed from SO_3 in F_2, heated again in E, catalyzed in O_1, again passed through V_1, and at last freed from SO_3 in F_1.

4. The gases purified in R_1 are heated in E, catalyzed in O_1, cooled in K, freed in F_1 from SO_3, heated in V_1, catalyzed in O_2, passed back into V_1, and again freed from SO_3 in F_2.

Otherwise the gases in modifications 2, 3, and 4 are treated as in 1. The temperature may also be regulated within the contact-spaces from the outside or inside (G. P. 113,932).

The main point in this new process is that more SO_3 is made with much less catalyzing substance without the necessity of strictly regulating the heat in the contact-space, and that the apparatus for cooling and purifying the gases is very much reduced, as most of the heat is taken out of them anyhow.

Recently a totally new style of working has been introduced, which combines the manufacture of SO_3 with complete desulphurization of the pyrites-cinders. If dry pyrites-kiln gases are passed over pyrites-cinders contained in a long tube, at a temperature of only 300° to 400° C., the surprising result follows that a great portion of the SO_2 has vanished in the issuing gas, without being replaced by an equivalent of SO_3. This evidently proceeds from the presence of ferrous compounds; for it was found that the above property of the cinders is multiplied by first impregnating them with ferrous sulphate. In that case the cinders retain the SO_2 very quickly and quantitatively. Now, if the cinders are heated more and more, always passing the roasting-gas over them, from 500° C., the exit-gases contain increasing quantities of SO_3 and also gradually increasing quantities of SO_2. Evidently the SO_2 formerly fixed is liberated in the shape of SO_3, without any SO_2 being freshly fixed in the cinders. If, therefore, a temperature above 550° is maintained for some time, the SO_3 in the issuing gases again quickly decreases and the ordinary catalytical process comes into action. It has been further found that in the case of ordinary pyrites-cinders the catalysis between 550° and 650° proceeds comparatively slowly, whereas cinders previously impregnated with ferrous sulphate exhibit a surprising increase of activity; most probably by the formation of Fe_2O_3 from the sulphates in a state of very fine division, as shown by the brick-red colour of the cinders treated in this manner.

If a little moisture is left in the kiln-gases, the SO_2 is fixed much more easily at lower temperatures. In that case the sulphur still present in the cinders in the shape of sulphide is burnt very completely and quickly, whereas the combustion is very slow with dry gases.

These observations have led to the following new process * :—Hot, undried pyrites-kiln gases are at once passed into a flue, in which pyrites-cinders, impregnated with ferrous sulphate, are carried continuously in the opposite direction, till the temperature sinks to 350°. In this case at the end of the flue a mixture of H_2SO_4 and SO_3 with excess of air escapes in a continuous stream, whilst on the other side the cinders come out entirely freed from sulphur. The process goes on as follows :—In the cooler zone of the flue, the SO_2 is retained by the cinders and the ferrous compounds contained therein; in the hotter zone the ferric sulphate formed splits up into Fe_2O_3 and SO_3. The newly formed Fe_2O_3 acts as a very good catalyzer and transforms part of the SO_2 into SO_3; at the same time the S still present in the cinders is burnt and increases the yield of SO_3, together with the $FeSO_4$ employed for impregnating.

This new process is entirely different from that described in the

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* U.S. P. by C. Krauss and R. M. von Berneck, No. 700,512, of May 20, 1902.

B. P. 17,266 (1898) of the Mannheimer Verein. In the latter the pyrites-cinders serve exclusively as catalyzer and are kept at as uniform a temperature as possible. Our process, however, is founded, firstly, on the sharply distinguished fixation of SO_2 and recovery of the same as SO_3, locally, and in point of time, separated from each other by cinders impregnated with ferrous sulphate, the fixation of SO_2 taking place at lower, the expulsion of SO_3 at higher temperatures, which must both be exactly regulated; secondly, on the artificially increased activity of the cinders. In the purely catalytic process the cinders need only be changed when they have partly lost their catalytic power in consequence of prolonged use (B. P. 1859 of 1898), whilst in our process the gases must be brought into contact with constantly renewed cinders in order to fix the SO_2.

In the catalytic process the desulphurization of the cinders comes into question only for a very small proportion of the cinders; in our process this is extended to the whole of them. In the catalytic process dry gases must be used and all moisture is rigidly excluded; in the new process, on the contrary, gases with a certain amount of moisture are preferred. In the catalytic process exclusively SO_3 is obtained, in our process a mixture of H_2SO_4 and SO_3.

Fig. 462 shows how this process can be carried out. Pyrites-cinders impregnated with ferrous sulphate are continuously moved forward in the channel C towards the pyrites-kiln. In the colder part of this channel (which may, if necessary, be cooled from without) the cinders take the SO_2 out of the kiln-gases which meet them and thereby gradually cool the gases, whilst the cinders are more and more heated up by the hot gases which stream in the opposite direction. At last, in the hottest zone the SO_2 formerly fixed is expelled in the shape of SO_3 by the hot kiln-gas. Thus at the hotter end of the flue continuously hot kiln-gases enter and desulphurized cinders fall out; at the cooler end continuously fresh cinders, impregnated with ferrous sulphate, are introduced, and cooled air, containing H_2SO_4 and SO_3, escapes which gives up the flue-dust carried along in chamber K_2. The cinders are put in by means of a chain of buckets and a feeding-worm. Channel C is a long iron tube, mechanically rotated. Inside, as shown in fig. 461, there are longitudinal ribs which bring the cinders into intimate contact with the gases and slowly convey them along to meet the gaseous current. The

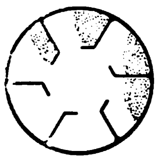

Fig. 461.

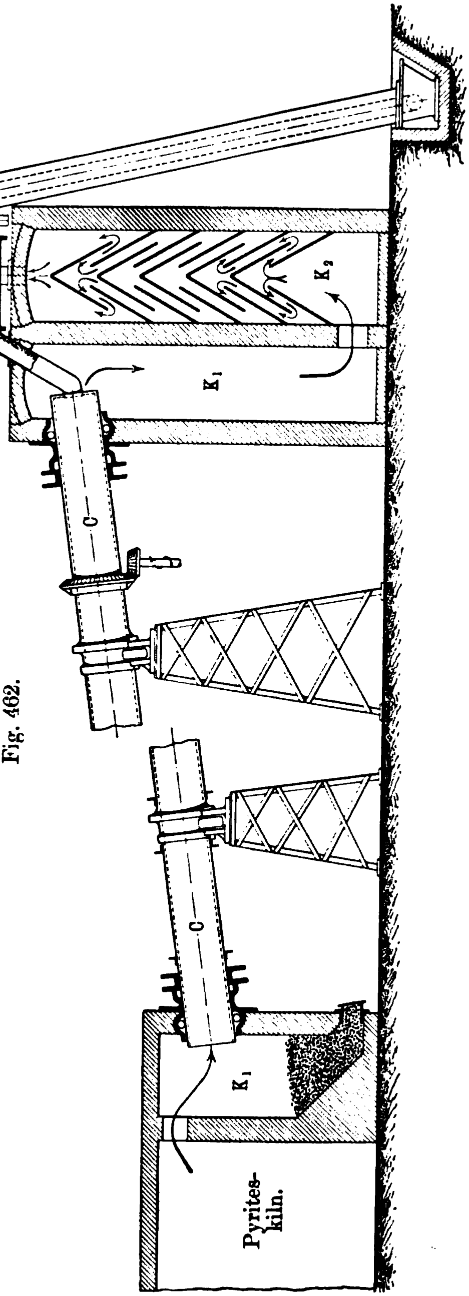

Fig. 462.

channel is, outside or inside, protected by an insulating mass in its hotter parts. The cinders may be used in the shape of dust or pieces; but cinders from lump pyrites are best broken up. The impregnation is preferably performed by the (rather troublesome) solutions of ferrous sulphate obtained in the wet copper extracting process, when operating without roasting the cinders with salt.

As to the manner in which the absorption of SO_3 is carried out at Höchst, I am enabled to make the following observations :—The absorbers are cast-iron vessels with outside cooling-jackets. The SO_3 gases are passed through the absorbing liquid in a state of extremely fine division, either by suction or by pressure. If hydrated sulphuric acid is made, only one absorber is employed: for fuming acid two or better three absorbers, placed at different heights. The absorbers are fed with acid of more than 93 per cent. H_2SO_4, if fuming acid is to be made; for hydrated acids they are fed with dilute acid or even pure water, run in by a lead pipe. Up to 95 per cent. the acid is as clear as crystal, above that strength it appears turbid through a slight quantity of iron salts taken up from the apparatus, which are insoluble in such highly concentrated acids and which cannot be removed either by settling or by filtration, but which vanishes on the addition of a slight quantity of water. Some factories mention this expressly in their sale notes for such extra strong acid.

A patent of the Farbwerke von Meister, Lucius, and Brüning (G. P. No. 135,887 of Feb. 7, 1902) shows how the platinum contact-mass, when *poisoned by arsenic*, can be made to recover its full activity without being removed from the apparatus. If *steam* is mixed with the hot burner-gases entering the apparatus, the contact-action is in the first instance lowered still further [through the poisonous action of water, comp. p. 1001]; but gradually the whole of the arsenic contained in the platinum as a fixed compound is converted into volatile compounds and escapes with the mixture of SO_2, O_2,SO_3, and H_2SO_4 issuing from the apparatus. The admixture of steam with the burner-gases it continued until no more arsenic can be traced in the condensing products; then the burner-gases are again introduced in the dry state and the platinum soon recovers its original activity.

III. *The Schroeder-Grillo Process.*

This process was invented by Dr. Schroeder and patented by him together with the Aktien-Gesellschaft für Zinkindustre vormals W. Grillo, B. P. No. 25,158, of 1898; 17,034, of 1900; and 10,412, of May 20, 1901.

Concerning this system, I have received the following communications from the inventor, Dr. Schroeder.

The difficulty of selling liquid sulphur dioxide (comp. p. 388) was the reason why the firm Grillo, already before starting the SO_2 plant, had taken into consideration the conversion of part of the SO_2 into sulphuric acid. The application of the lead-chamber process did not seem to be the right thing in this case, because the dilute acid to be manufactured in this way had too low a market value.

On the other hand, the fuming sulphuric acid obtained by contact-processes was at that time still rather expensive, because the preparation of gases, containing much SO_2, according to Winkler's process of decomposing sulphuric acid, offered technical difficulties, whilst the direct application of roasting-gases, so far as was publicly known, had not yielded satisfactory results.

Under these circumstances the pure sulphur dioxide made at Hamborn from roasting-gases appeared to be an advantageous starting material for the preparation of rich and pure gaseous mixtures for the contact-process. At the request of the firm Grillo, the Badische Anilin- und Sodafabrik at their Ludwigshafen contact-plant made some experiments with gaseous mixtures prepared from Hamborn liquid SO_2 with admixture of air, but the result was not satisfactory.

But as in the meantime laboratory experiments made at the Hamborn zinc-works by Haenisch and Schroeder had yielded very good results with a comparatively high working capacity of platinum, the firm Grillo resolved to erect an experimental factory for the further development of the contact-process. The starting idea was the assumption that the formerly unsatisfactory results of the contact-process had been principally caused by the fact that the contact between the gases and the solid reacting medium was not sufficiently intimate for converting approximately all SO_2 molecules into SO_3. The aim was therefore to prevent the gaseous molecules from slipping past the active platinum substance, by means of filling the reaction-space as completely and evenly as possible; and as the ideal state of arranging the platinum molecules suspended at equal distances throughout the reaction-space was naturally impossible to realize, there was no other way of dividing the platinum than that formerly universally applied, viz.: spreading the platinum upon porous substances hardly at all active by themselves, and employing these for filling the reaction-space. In practice, deviating from the formerly preferred loose packing of the platinized substances, principally platinized asbestos, this packing was made very firm.

The wrought-iron contact-pipes, 6 inches wide and 13 ft. 1½ in. long, were filled as follows:—On a bottom of fine stone material a dense plug of platinum asbestos (8 to 10 per cent. Pt) was placed, and firmly compressed by means of a disk fixed to a long rod. In order to exclude the formation of continuous channels, another layer of stone was put in, and again a firm asbestos plug of about 3 inches height. About 15 double layers of this kind were placed in each pipe, the first portion of the pipe remaining free for a preliminary heating of the gases. A group of five pipes was placed in a furnace in such a manner that the first empty portion lay in the fireplace itself and the second portion, packed as above, was surrounded by the gases issuing from the fireplace. The temperature of the furnace decreased from front to back, and was regulated by means of a pyrometer in such a manner that in the centre a temperature of 400° to 420° C., which had been found most favourable for the reaction, was obtained. As the resistance of the contact-mass was bound to be very great, the proportion of the gases was not effected by the hitherto usual fan-blast, but by a cylindrical air-compressor, arranged so that it produced at the same time a mixture of SO_2 with atmospheric air in the suitable proportion of 25 vols. SO_2 to 75 vols. air (B. P. 9188, 1887).

The working of the plant showed that the resistance of the contact-mass, with a normal gaseous current, was equal to 0·8 to 1 atmosphere, a somewhat considerable amoumt, but that, on the other hand, in consequence of the intimate contact of the gases with the platinum, the degree of conversion greatly exceeded all former results. Each contact-pipe produced about 300 to 400 kils. SO_3 per diem, the yield being about 95 per cent. of the theoretical.

The German patent No. 42,215 had also provided for applying a greater pressure than necessary for overcoming the resistance of the contact-substance in order to prolong the stay of the gases in the contact-space and to favour the union of the active molecules of gases; but this was found superfluous in the experimental plant and was never applied in the plants subsequently erected.

On the strength of the favourable results obtained with the Hamborn experimental plant, the Badische Anilin- und Sodafabrik in 1887 resolved to carry out the process on the large scale, the firm Grillo renouncing the manufacture of SO_3 for a space of ten years. Apart from the plant erected at Ludwigshafen in 1887, which has worked for some years, several smaller plants on the same system have been erected by other firms, many of which are even now at work without any change in the contact-action *.

When in 1897 the field was again clear for the firm Grillo, it was resolved to start the contact-process again at the Hamborn zinc-works. The old experimental furnace was re-erected, and it was found that the conversion, when employing roasting-gases with 5 to 7 per cent. SO_2, was at least as good as with the rich gases formerly used. Thereupon the firm (now "Aktien-Gesellschaft für Zinkindustrie vormals Grillo"), together with Dr. H. Schroeder, started arranging the process for the direct working of blende-roasting gases. As with these dilute gases the process could only pay when greatly reducing the resistance of the contact-mass to the propulsion of the gases, without reducing the yield, efforts had to be made to find a sufficiently porous and resisting contact-mass. It had also to be taken into consideration that the danger of a diminution of the contact-action in the case of roasting-gases, even when these are well purified, is much

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* According to direct information from the Badische, their experiments with the Grillo process were made with inefficient plant and could not be held to be conclusive in any way. Before treating with the firm of Grillo, since 1881, they had already commenced experiments with ordinary burner-gases, and their contract with Grillo did not in any way prevent that firm from working in the last-named direction at any time, even before 1897.—G. L.

greater than with absolutely pure mixtures of pure SO_2 and filtered air. It was already known by experience that platinum asbestos, with perfectly pure gases, has an infinitely long action, but that its catalytic action gradually decreases when imperfectly purified gases are employed, and that there was then no means of regenerating its action except by the very troublesome process of transferring the platinum upon fresh asbestos.

This difficulty of regeneration led to abandoning the hitherto employed substrata for platinum in favour of soluble salts, where, owing to the easy renewal of the surface and the porosity of these substances, the regeneration was bound to be much easier than in the case of platinized asbestos, pumice, and the like.

It was soon found that in this way not merely contact-substances of great porosity and easy to regenerate could be obtained, but some of these salts, *e. g.* magnesium sulphate, yielded contact-substances of decidedly better catalytic action than asbestos, pumice, and the like. These contact-substances, protected by patents in all countries (B. P. 25,158, of 1898), can be made in a very simple manner by mixing or soaking the salts with a dilute platinum solution. The platinum is reduced, without the assistance of other substances, by passing the hot gases containing SO_2 over the mass; but of course the reduction may be hastened by the admixture of organic substances, such as sugar, oil, glue, &c., afterwards burned, and the porosity of the mass is thereby at the same time increased.

To decrease the resistance against the passage of the gases, much larger pipes are now employed. But as the activity of the platinum was found not to be fully utilized, greater dilutions of platinum in the magnesium sulphate masses were employed; less than one-hundredth of the percentage of platinum formerly employed is sufficient without any detriment to the contact-action. Afterwards, in lieu of a number of pipes, a single contact-chamber was introduced, as already described in Deacon's patent, Nos. 753 and 1682, of 1871 (comp. *suprà*, p. 980). The apparatus was constructed in such a manner that the SO_2 gases were first heated up to the requisite temperature in a tubular apparatus and then passed into the contact-space. As the reaction proceeds vividly, a quantity of heat being set free by itself, the contact-apparatus need not be heated but merely protected against radiation. But the yield in these apparatus was found to be only 85 to 90 per cent. of the theoretical. Although on principle a preliminary heating of the gases to 250° C. ought to suffice, since the formation of SO_3 commences to set in just over 200°, and more and more heat is generated by the reaction itself, it was established by gas-analyses and temperature determinations that the reaction progresses only in the centre of the cylinders, whilst the gases rising near the walls, in spite of good insulation, lose more heat than can be spared for the reaction *.

This drawback could be avoided by a compulsory mixture of the gases in simple or composite cylinder apparatus, as described in the B. P. 17,034, of 1900. These apparatus have been found to answer very well and to act in no way inferior to the composite pipe apparatus. The resistance of the contact-mass to the propulsion of the gases can be reduced by a suitable increase of section in such a way that revolving apparatus (fan-blowers) are quite sufficient for that purposes.

A further improvement in the contact-mass was attained by building up the mass in the molten state in the contact-apparatus itself by means of a hot current of gas or air (B. P. 10,412, of 1901). Thus not merely a high degree of porosity is attained, but the caking of the mass prevents the strong gaseous current from carrying away single portions of it.

The absorption of the vapour of SO_3 formed takes place after cooling in iron apparatus by means of sulphuric acid, either by surface-action or submersion or running the absorbing acid down a tower or spraying it in the stream of SO_3 vapour. If no dilute sulphuric acid for this purpose is yielded by another part of the works, it is prepared by mixing part of the strong acid previously obtained with water and cooling.

For cooling, purifying, and drying the roasting-gases before introducing them into the contact-process in many cases the process prescribed by Rath (G. P. 22,118) has been found sufficient, consisting in slowly filtering the gases through coke moistened with sulphuric acid. The low velocity of the gases, at most 2·3 inches per second, requires a very wide section of the low towers and admits of employing a very fine coke-packing,

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* The apparatus erected at Ludwigshafen for the Grillo-Schroeder system by Dr. Schroeder himself did not work as above, but was expressly arranged to keep the temperature of the outer contact-oven as uniform as possible at all points.—G. L.

without any considerable resistance to the passage of the gases. In order to increase the filtering action, it is possible to employ apparatus containing a fibrous material like asbestos or cotton-wool. Such a purification in connection with drying the gases by sulphuric acid is quite sufficient for the removal of flue-dust, mist, sublimates, and moisture from the gases, but not for purifying the gases from injurious gaseous constituents evolved in the roasting of some ores. The most injurious of such gases has been found at Hamborn to be silicon tetrafluoride evolved in the roasting of ores containing fluorine. Unless previously removed, that gas is decomposed within the contact-mass in such a manner that dense layers of silica are formed which envelop the contact-substance and render it inactive.

Apart from silicon tetrafluoride, arseniuretted hydrogen must be taken into consideration, whose injurious action upon the catalytical property of platinum has been long known. At Hamborn and in many other places that gas has not been noticed, probably because the conditions of its formation (application of iron gas-pipes, &c.) were not present. The sublimed As_2O_3 contained in the gases is easily removed by filtration together with the other constituents of flue-dust.

If in consequence of insufficient purification of the gases the contact-action is gradually weakened, the contact-mass must be from time to time freshened up, especially in order to counteract the incrustation with silica. This is most conveniently done by washing the mass with a dilute solution of aqua regia, whereby the platinum is freed from the surrounding silica, and at the same time the porosity of the surface is renewed. Any slight traces of arsenic absorbed by the contact-mass are equally removed by the aqua regia, being converted into $AsCl_3$, which volatizes in the hot current of air when heating up the contact-mass.

If ultimately the percentage of silica, iron, &c. becomes so large that the regeneration in the just-mentioned manner is not sufficient, the platinum and the salt must be separated from the impurities in the wet way.

In the beginning of 1902, ten factories were working the Grillo-Schroeder process (four of them in Germany), and another twelve factories (again four in Germany) were in course of erection.

Thus far I have translated verbatim Dr. Schroeder's communication; I shall now subjoin abstracts of the various patents taken out for this process.

Grillo and Schroeder (Engl. pat. 25,158, of 1898) produce a contact-mass by an intimate mixture of a soluble salt not changed by the agents in question, such as sulphates or phosphates, with finely divided platinum in the following manner:—The salt (*e. g.*, sodium sulphate) is dissolved in water, mixed with platinic chloride in the proper proportion, and the whole evaporated to dryness, breaking up the crusts so formed into pieces of uniform granular size. The separation of the platinum in a metallic state, of very high grade of division, takes place on heating the contact-mass when the process is started. These contact-masses act perfectly well even when containing only 0·1 per cent. of platinum, and when rendered inactive they are simply dissolved in water, whereupon the platinum separates out in a metallic state and can be employed over and over again.

Their German patent No. 115,333 describes the removal of arsenic, antimony, mercury, &c. from the contact-mass in the contact-space itself by means of a current of chlorine at the ordinary temperature of that space or somewhat below. Previously, any oxides of those metals present may be reduced to the metallic state by means of coal-gas, carbon monoxide, &c.

A further patent, E. P. No. 17,034, of 1900, by the Aktien-Gesellschaft Grillo and M. Schroeder gives the following prescriptions:—Pyrites-kiln or similar gases, with about 6 per cent. SO_2, pass into the bottom of a chamber, where they are heated to 260° or 280° C., thereupon through several layers of contact-substance spread on perforated iron plates, and from this, now in the state of SO_3, to the absorbers. The perforated metallic diaphragms produce a good mixture of the gases and a uniform temperature which is controlled by laterally introduced pyrometers. The temperature during the reaction may rise to 500° or 520°, the gases leave at 350° or 400° C. A larger style of apparatus consists of several vessels connected by pipes, alternately above and below the layer of the contact-substance. The mixture of the gases passing from any one chamber to the next in series is promoted by causing them to flow through a narrow passage into a larger space before traversing the contact-matter next in turn. In this manner a conversion of 96 to 98 per cent. is said to be effected in place of only 85 to 90 per cent. where such distribution is not employed, in consequence of excessive heating in the centre and cooling below the proper temperature at the walls.

The claims under this patent are as follows:—

1. In the catalytic process of making sulphuric acid or its anhydride without regulating the temperature of the reaction from the outside, the use of a contact-apparatus consisting of a vessel or chamber provided with solid partitions having one or more openings through which the preheated or flowing contact-gases are constrained to pass after they have passed through a quantity of contact-mass for the purpose of being thoroughly mixed previous to passing into another quantity of the contact-mass.

2. For the purpose referred to in claim 1, a contact-apparatus consisting of a number of vessels charged with contact-mass and connected by pipes in such a manner that the gases in passing from one vessel to the adjoining one are thoroughly mixed.

A still more porous mass than usual is obtained by Grillo and Schroeder (E. P. 10,412, of 1901) by forming the pores in the "carrier" whilst this is still in the pasty condition and in the process of drying, by forcing a gaseous current through the mass at a rate similar to that employed in the converter during normal working. Suitable substances as "carriers," apart from the salts mentioned in the patents, are clay, gypsum made into a paste with water, also salts melting in their own water of crystallization. The preparation of the contact-mass may be carried out in the contact-oven itself. (A German patent by Neuendorf, No. 127,846, runs on similar lines, employing salts of Ca, Ba, Si, other than the sulphates, with SO_2, air, and steam, or sulphuric-acid vapour at a high temperature.)

Quite recently several important contributions concerning the Schroeder process have been made to the New York Section of the Society of Chemical Industry, and are published in its Journal, 1903, pp. 348 *et seq.*, by Fr. Meyer, G. C. Stone, and C. L. Reese. The first of these is of a historical kind and adds nothing of importance to what has been said before on that process. I here give an abstract of the other two papers.

Stone points out that in the Schroeder process the following impurities are most injurious: arsenic (which does not occur in the blende used at the original works at Hamborn), SiF_4, HCl, and Cl. Arsenic permanently ruins the contact-mass, the other impurities have only a temporary effect which vanishes when pure gases are used. With properly purified gas the mass gives a yield of 96 per cent. and more even after a year's run. When it is necessary to regenerate it, it is spread on a cement floor, made into a stiff paste with a mixture of dilute nitric acid, hydrochloric acid, and sugar, allowed to stand for a few days, heated to expel water and acids, cooled and crushed. It is then often slightly better than when first used.

There are at present 23 Schroeder plants built or building (7 in Germany, 2 in Russia, 1 in Poland, 1 in Italy, 2 in France, 1 in Chili, 1 in Mexico, 2 in South Africa, 6 in the United States). Some are using blende, some pyrites, some brimstone, and one a low-grade gold-ore. Their degree of purity being very different, different methods of purification are used. In every case there is a dust-catcher next to the burners, then a cooler by which the temperature is reduced to that of the air, then scrubbers or washing-towers for washing and drying the gas, then filters for removing most of the arsenic, selenium, &c. The gas is drawn from the filters and forced through the preheaters, in which it is got up to 300° to 400° C., when it immediately enters the converter. There is no necessity for regulating the temperature in the sectional converters, which are sometimes large enough to produce 10 tons acid of 66° B. in one day. From the converter the gas passes to a cooler, where it is cooled down to about 50° C., and then to the absorbers. When only acid of less than 100 per cent. H_2SO_4 is to be made, some form of scrubbing-tower is the best absorber; for fuming acid horizontal cylinders, followed by a tower, are most suitable, and acid up to 40 per cent. free SO_3 can be made here directly. Every hour the SO_2 in the entering and exit gases is estimated by the Reich test. The purity of the gases is best ascertained by blowing a small current of the gas continuously through a tube filled with absorbent cotton, which ought not to show a deposit or discoloration after several weeks.

The conversion is good and uniform, *e.g.* at one plant for a month's run minimum 94·47, maximum 97·76, average 96·68; at another in 77 days' run minimum 91·48, maximum 97·43, average 95·39 per cent. It remains the same whether the gas contains only 3 to 4 per cent. or 6 to 7 per cent. SO_2. The stops from all causes do not exceed 20 hours per month. The acid made was 95·01 per cent. of the sulphur burned. The cost of the plant is less than that of a lead chamber and concentrating-plant.

For acid above 60° B. the process is cheaper than chambers; from 60° B. below there is no advantage. A plant is now being built for combining the Schroeder process with chambers, so as to produce strong acid without concentrating-plant.

Reese describes his experimental investigations on the Schroeder process. His results are most interesting, but partly differ so much from those of other observers that further observations seem called for. Thus he states that the gases need not be dried, but may even be saturated with moisture without affecting the conversion in any way, although this cannot be carried out in practice owing to the necessity of using iron pipes. CO_2 and CO have no effect, nor has sulphur in a finely divided form. HCl reduces the conversion at once to 42 per cent., Cl to 57 per cent.; SiF_4 acts similarly: but in all these cases, if pure gas is introduced, the conversion gradually rises again to the normal point. Arsenic is extremely injurious; it may reduce the contact-action to zero, but it can be removed from the contact-mass by a stream of HCl, best mixed with SO_2 (burner-gas). It is found in the shape of a *mist*, together with $PbSO_4$, SiF_4, HCl, S, and Se. This mist cannot be removed by scrubbing with either water or sulphuric acid, but by wet filters [evidently made of asbestos or cotton-wool, comp. below]. By these the gas is purified to such an extent from solid and liquid substances that a beam of sunlight from a lens cannot be seen when passed through a vessel containing the gas [Tyndall's test]. In this case the contact-mass lasts indefinitely. Another test is to allow the gas to pass continuously through a tube containing absorbent cotton, when any acid or other impurity can be seen after a short time deposited on the cotton [comp. *suprà*].

The reaction starts at 330° to 340° C., and is at its best at 425°, but there is very little difference between 400° and 435° C. With impaired contact-mass a higher temperature is required to start the reaction. No cooling is necessary with the Schroeder contact-mass when used in sectional converters, otherwise than that resulting from radiation. It is simply necessary to preheat the gas to about 400° C., and the converters do the rest. 85 to 90 per cent. of the conversion takes place in the first of the four sections, where the temperature rises about 100° C.; it gradually falls in the other sections and gases leave the converter below the temperature at which they enter.

The absorption of SO_3 by water is not so good as might be expected. The rate of absorption increases with the strength of the sulphuric acid formed, and is at a maximum when the vapour-tension is zero. Evidently SO_3 unites with the vapour of water, forming minute globules of H_2SO_4, which cannot be satisfactorily absorbed by acid of any strength or even alkali, but perfectly by means of several layers of wet asbestos or cotton-wool.

IV. *The Process of the Mannheimer Verein.*

Previous to describing this, we shall say a few words as to the steps which have led to the introduction of *oxide of iron* as a contact-agent.

We have seen before (p. 978) that oxide of iron was a long time ago recognized as a catalytic agent, capable of bringing about the combination of SO_2 and O to SO_3, and that experiments of utilizing this property had been made pretty early on a large scale but unsuccessfully. We have also seen (p. 402) that, on the other hand, sulphur trioxide was recognized as being present in ordinary pyrites-kiln gases, and that it has even been proposed to utilize this SO_3 as such without any further change (p. 971).

I had myself contributed to the elucidation of this subject and found that the quantity of SO_3 in the burner-gas would be considerably increased by passing the gas through a layer of red-hot pyrites-cinders, *i. e.* ferric oxide (Berl. Ber. 1878, x. p. 1824, and Chem. Zeit. 1883, p. 29). I then got up to a conversion of 18 per cent. of the SO_2 into SO_3, and I did not pursue the subject any further, because my professed object was attained—viz., to study the process going on in the pyrites-kilns, and to explain the formation of SO_3 therein,—and it did not strike me that, by increasing the duration of the action, a process for making SO_3 on the large scale might be worked out on that foundation. This was perhaps detrimental to my interests, but I certainly do not deserve the accusation brought against me in the G. P. 107,995 that I had declared the question of the applicability of ferric oxide as contact-substance for making SO_3 on the large scale as settled in the negative by my experiments, and that I had thereby misled other enquirers. In Zsch. für angew. Ch. 1900, p. 80, I have disproved this assertion, and those concerned have never said anything more about it. On the contrary, it is clear that my publications had indeed induced others to follow up the subject in the manner we shall describe later on.

We now come to the process actually practised at Mannheim, which is the invention partly of Dr. Hasenbach, partly of Dr. A. Clemm, both of the Verein chemischer Fabriken at Mannheim.

The patents are:—B. P. (Verein) No. 17,266, Aug. 10, 1898; (Verein) No. 1859, Jan. 26, 1899; (Verein) No. 3185, Feb. 13, 1899; (Clemm) No. 15,151, July 22, 1899; (Verein & Clemm) No. 24,748, Dec. 12, 1899; (Verein & Clemm) No. 4610, 1901; (Verein) No. 18,206, of 1902. U.S. P. (Clemm & Hasenbach) No. 690,133, Dec. 31, 1901.

This process is also carried out at Ardeer (Scotland) and in other places.

The following original communication concerning that system has been made to me by the Verein chemischer Fabriken in Mannheim:—

"The principles underlying our process are as follows:—1st, roasting the pyrites with dried air, in order to produce dry kiln-gases. 2nd, graduated conversion of sulphur dioxide into sulphur trioxide in two separate contact-spaces, one of which is charged with ferric oxide, the other with platinum. The SO_3 formed in each of these is best absorbed in separated absorbing-plant. 3rd, behind the absorbing-apparatus for the SO_3 formed in the ferric oxide contact-space there is a filter for retaining from the gases any impurities injurious to the platinum contact.

"These principles are embodied in our patents [quoted *suprà* and abstracted below]. The apparatus constructed for carrying them into practice consists of a pyrites-kiln, differing from ordinary pyrites-kilns by being completely cased in iron and by such a construction of all openings that the doors can be tightly pressed against faced frames, in order to prevent as much as possible the entrance of undried air through the brickwork and the working holes.

"The air necessary for burning the pyrites is introduced by means of pipes underneath the grates. This air is dried in towers fed with concentrated sulphuric acid. The roasting-gases enter still hot into a perpendicular iron-cased chamber, filled with ferric oxide in pieces, to a height of 7 to 10 feet. This oxide [pyrites cinders] rests on a revolving grate, by which the spent contact-mass can be removed, the fresh contact-mass being fed in at the top. Here the conversion of the SO_2 into SO_3 is brought about to the extent of 60 or 65 per cent., and at the same time the arsenic is chemically fixed by the ferric oxide.

"From this chamber the gases enter into cooling apparatus and thereupon into absorbers, where the SO_3 formed by the ferric oxide contact is retained. At the end of the absorbing-apparatus a fan-blast is placed which draws the gases through the various apparatus hitherto described, and propels them through the following apparatus. The gases at this stage are very pure, but they contain still traces of impurities, not shown by chemical analysis, which in course of time might injure the activity of the platinum contact-substance, and small quantities of uncondensed sulphuric acid [anhydride], which must be removed before the gases act upon the platinum.

"This purification of the gases is brought about by filtration through porous, granular, or fibrous substances. After having been thus filtered, the gases possess such a degree of purity that the activity of the platinum contact-mass is secured for a very long period. The filtered gases are heated up by the heat of the kiln-gases or by a direct fire to the degree necessary for the reaction and now enter the platinum contact-space, in which the remainder of the SO_2 is converted into SO_3. From here the gases pass through a cooler and into an absorber, where the newly formed SO_3 is retained, and ultimately into a chimney."

We shall complete this sketch by abstracts of the patent specifications.

B. P. 17,266, of Aug. 10, 1898, prescribes burning pyrites in ordinary furnaces, to which air is admitted previously heated and thoroughly dried. The hot roaster-gases are at once conducted over a contact-substance containing ferric oxide (preferably fresh burnt pyrites-waste) placed in an oxidation chamber to which external heat is not applied. Pyrites-waste affords also an excellent means for extracting, in a technically perfect manner, the arsenic from pyrites-kiln gases, so that a large yield, free from arsenic, is obtained from the initial materials containing arsenic, if, in passing the gases over the burnt ore, the production of comparatively large quantities of sulphuric acid be as much as possible avoided.

B. P. 1859, of Jan. 26, 1899, describes the chambers for containing the burnt pyrites with their revolving grates, their iron casing, and their devices for excluding all air except that which has been desiccated.

B. P. 3185, of Feb. 13, 1899, describes another modification of contact-furnace, with more admission of air. The ordinary roasting-gases, containing 6 or 8 per cent. SO_2, are to be diluted with desiccated air, either when in the reaction-chamber or before entering it, so as to produce a gaseous mixture containing from 2 to 3 per cent. by volume of SO_2, whereby the production of SO_3 is considerably enhanced.

According to A. Clemm's B. P. 15,151, 1899, a mixture of SO_2 and O or acid is passed over red-hot copper sulphate, previously moulded into convenient forms with clay or gypsum.

A. Clemm and the Verein chemischer Fabriken in Mannheim (B. P. 24,748, 1899) conduct the gases from the pyrites-kiln, with admission of dried air, over highly heated burnt pyrites, then subject them to dry filtering over pumice-stone, asbestos, or the like, and afterwards admit them to a second contact-apparatus, charged with platinum contact-substance. The SO_3 formed in the first contact by the action of ferric oxide may be absorbed before passing the gases on to the platinum contact-chamber. (This seems to be essential, in order to prevent deterioration of the platinum catalyzer, the gases being reheated if necessary.) The platinum contact-mass is preferably platinized grating or network or platinized fabric carried by frames. The Verein, in B. P. No. 18,206, of 1902, describes an apparatus charged with platinum asbestos so arranged that the contact with the gases is as perfect as possible, without employing much pressure.

The Mannheimer Verein chemischer Fabriken (E. P. 4610, 1901) also patents the use of copper oxide, chrome oxide, or manganese oxide, or a mixture of the three, or their sulphates, as contact-substances and also for filtering the hot roasting-gases.

We shall lastly describe more in detail the pyrites-kilns and contact-chambers. In figs. 463 & 464, a_1, a_2, a_3, a_4 are burners, b the pyrites burning therein. All openings are made tight by asbestos joints and screw-bolts, the doors being pressed against planed surfaces; this is shown at c. The air enters at d_1, d_2, in drying-towers e_1, e_2, and is carried by pipes f_1, f_2, f_3, f_4 underneath the burner-grates. Further pipes, f_5, f_6, communicate with the contact-chamber, in case this is equally to be supplied with dried air, and in a similar manner this can be supplied over the layer of burning pyrites. The gases issuing from the burners traverse upright chambers, g_1, g_2, filled with pyrites-cinders, where the conversion of SO_2 to SO_3 takes place; they are then taken by *h* to the condensing-apparatus. The whole furnace is cased with iron, in order to prevent any air from penetrating through the brickwork. Through *k* fresh pyrites-cinders are charged into g_1, g_2, and through the revolving grate *j* the spent cinders are removed. Further openings may be provided in the burner or contact-chamber for diluting with air. The air is preferably heated before entering the apparatus.

Fig. 463.

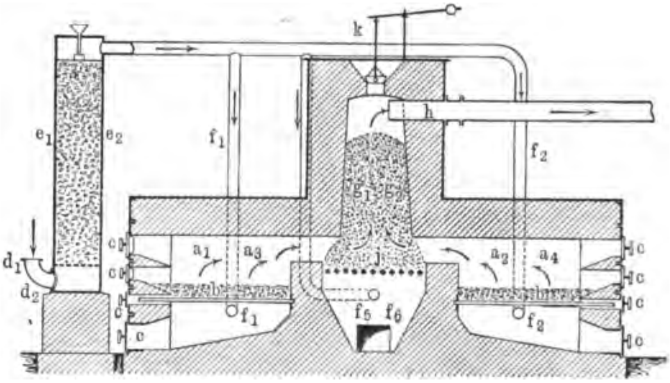


Fig. 464.

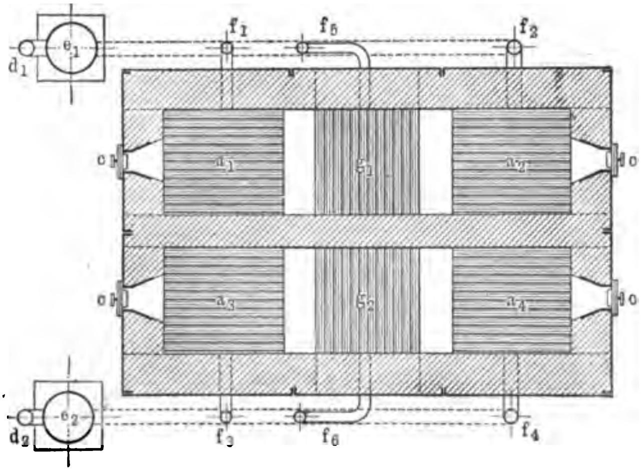


Fig. 465.

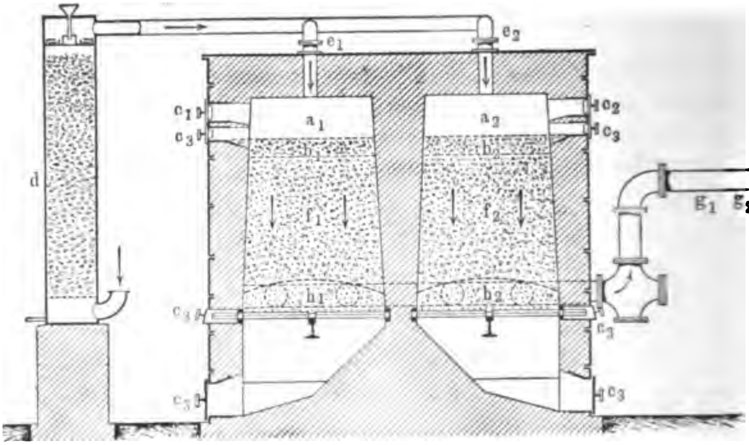


Fig. 466.

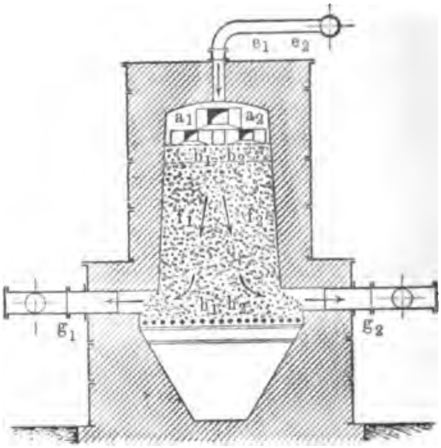


Fig. 467.

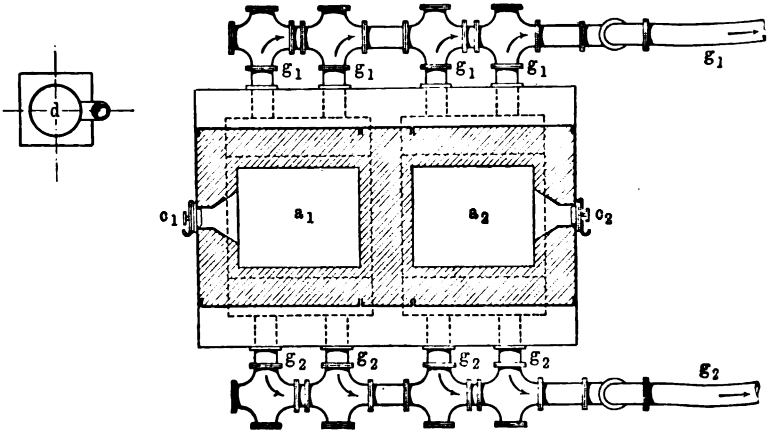


Fig. 465 to 467 show how the contact-chamber may be placed underneath the burners, and is traversed by the burner-gases from the top downwards. In a_1 and a_2 the burning takes place; b_1 and b_2, the burning pyrites; c_1 and c_2, the air-tight charging-doors; c_3, the other working-door, equally air-tight. In this case the pyrites burns from the top downwards. The necessary air is dried in tower *d* and passed into the apparatus through pipes e_1 and e_2. The gases generated in layers b_1 and b_2 pass through the layers of burnt ore f_1 and f_2, where the conversion of SO_2 into SO_3 takes place, and then go through g_1 and g_2 to the condensers. The spent oxide is removed by the revolving grates h_1 and h_2. This furnace must also be cased in iron.

Experiments made by Lunge and Pollitt (comp. *suprà*, p. 1008) have confirmed the fact that the degree of conversion of SO_2 into SO_3 is strongly reduced by the least amount of moisture present, either in the ferric oxide or in the gases. This degree remains the same, whether the gases contain up to 13 per cent. or down to 2 per cent. SO_2 by volume. The best temperature for the reaction is about 620° C. The presence of copper oxide or arsenic (which is no doubt converted into ferric arseniate) increases the catalytic action, the arsenic more than the copper. Probably the SO_2 is first oxidized to SO_3 at the expense of the arseniate, and the arsenite thereby formed is again oxidized to arseniate by atmospheric oxygen. (This influence of arsenic in promoting the contact-action, found by Lunge and Pollitt, forms the subject of a German patent applied for by the Mannheimer Verein chemischer Fabriken.)

V. *The Freiberg Process.*

Through the kindness of Professor Clemens Winkler I am enabled to give the following new and authentic communications on the introduction and development of the manufacture of sulphuric anhydride by the contact-process in the Muldenerhütte at Freiberg, on the strength of official documents, all of which have hitherto remained unpublished.

The first experiments for carrying out the process of combining SO_2 and O by means of the process published by Winkler in 1875 (Dingler's Journal, ccxviii. p. 128) on a manufacturing scale began on December 18, 1876. As described in that publication, sulphuric acid of 66° B. was decomposed by strong heat, the resulting gaseous mixture was dried and conducted over moderately heated platinum asbestos. The SO_3 thus obtained was at first condensed as such, later on much more conveniently by absorption in concentrated sulphuric acid.

The results were so satisfactory that on March 9, 1878, the erection of a larger plant was resolved upon. But almost exactly at the same time, on March 10, 1878, the Royal Mining Office received a report by Cl. Winkler, in which he requested them to take notice of an observation made by him which would enable the process of manufacturing anhydride to be carried on in a new and much more practicable form. This report contains the following passage:—"*The undersigned has succeeded in achieving a result regarded as impossible according to former experiments, viz. the production of sulphuric anhydride from a mixture of sulphur dioxide and atmospheric air.* After discussing at length the points important for the success of the new process, the author gives a description of the *way in which the process can be carried out on the large scale.* He here discusses, first, the quality of the gaseous mixture obtained in the kilns; secondly, the mode of propelling the gases; thirdly, the purification and drying of the gases; fourthly, the transformation of SO_2 into SO_3; fifthly, the condensation of the SO_3.

The production of sulphuric anhydride from pyrites-kiln gases at the Freiberg works commenced on a small scale in the beginning of December, 1878, on a larger scale on February 1st, 1879. But as there were many difficulties to overcome and many changes became necessary in the plant, the commencement of a continuous manufacture dates only from December 13, 1879. On October 3, 1881, a larger plant was started, utilizing a proposal found successful in the meantime, for removing the last traces of flue-dust (which interferes with the efficiency of the contact-substance) by filtering the gases through carded cotton-wool.

Soon after the Freiberg works had commenced trying the manufacture of SO_3 from kiln-gases, the Rhenania works at Stolberg entered upon this path, with mutual understanding and partial exchange of experiences. At Stolberg, vertical contact-apparatus was preferred to the horizontal pipes used at Freiberg. The filtration by cotton-wool and the employment of platinized porcelain (see below) has also remained a speciality of the Freiberg works.

The manufacture of sulphuric anhydride is now carried out at the Muldenerhütte, near Freiberg, as follows:—

1. *Roasting-gas.*—Since 1879, the gases from ordinary pyrites-kilns, containing a little arsenic have been employed for this purpose.

2. *Propelling of the gas.*—Since 1879 this has been effected by a steam-driven fan-blast placed between the purifiers and the contact-apparatus, so that the gas is aspirated from the kilns through the purifiers, and propelled under pressure into the contact-pipes and the absorbing-towers.

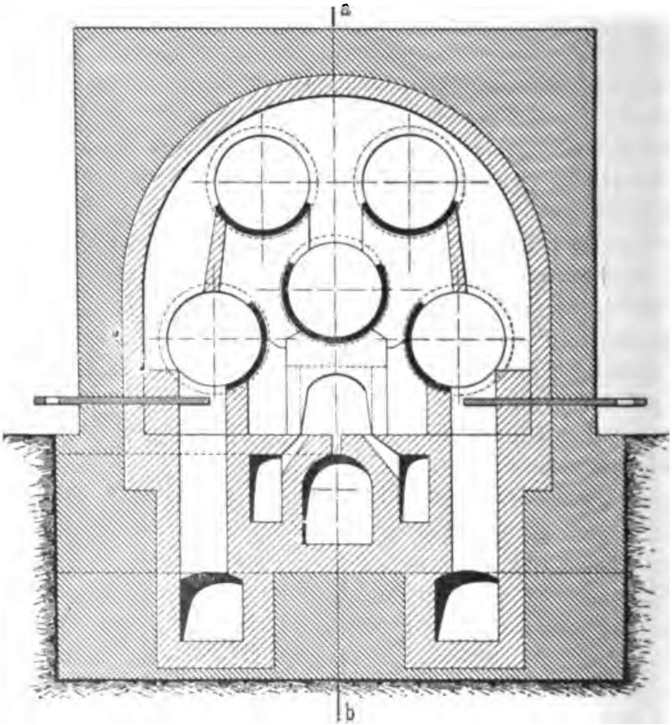
3. *Purification of the gases.*—This is effected *exclusively by filtration*, without any *washing-* or *drying-apparatus.* This has been done since 1881, ultimately through the employment of carded cotton-wool, which retains the last traces of flue-dust without the necessity of frequent renewal (probably gun-cotton might be employed for the same purpose). At first it was thought necessary to wash and dry the gases, after previously removing most of the flue-dust, by towers fed with sulphuric acid of 66° B.; but this caused the cotton-wool to be gradually moistened and destroyed by the slight quantity of sulphuric acid carried away by the gaseous current, so that frequent renewals of the somewhat costly filtering materials became necessary. Since 1893, part of the cotton-wool has been replaced by cheap fine wood-shavings ("Holzwolle"); in 1896 the washing with sulphuric acid was curtailed and in 1898 it was entirely abandoned. Since then the moistening of the wool has ceased; it retains its porosity and therewith its efficiency. The gases have since been purified without the assistance of liquids, exclusively in the dry way, and that with such perfection that the contact-substance retains its activity for years. Practically the process is performed as follows:—The gases, as they come from the kilns, are passed through leaden flue-dust tunnels, where most of the dust is deposited, afterwards through a set of lead towers, packed successively with coke, charcoal, wood-shavings, and cotton-wool. From the last tower the gas, absolutely free from dust, is aspirated by the fan-blast and propelled with moderate pressure into the contact-ovens.

4. *The contact-substance.*—From 1879 to 1883 *platinum asbestos* with 40 to 50 per cent. platinum was used, prepared by means of sodium formiate (p. 1086). In consequence of the impurities, at that time still present in the gases, the platinum asbestos soon became inactive, especially by incrustations of sulphates, and had to be frequently worked over again in a troublesome manner. In 1883 the transition was made to *platinized pumice,* containing 3 or 4 per cent. platinum, whose activity lasted up to a year. In 1888 this was replaced with excellent results by unglazed *platinized porcelain.*

5. *The temperature of combination.*—According to the experiences made at Freiberg, the union of SO_2 and O is best effected at a temperature of 440°–460° C. as measured by a Heracus (Le Chatelier) pyrometer. The inside of the retort-furnace is faintly red-hot, but at 440° the red sheen ceases. Any effect of the heat of reaction upon the temperature could not be noticed.

6. *The degree of combination.*—During the first ten years of working the degree of combination attained was imperfect. The SO_2 percentage of the kiln-gases, originally 7 to 7·5 per cent., was diminished to about 4 per cent. SO_2, equal to a conversion of about 45 per cent. into SO_3. This did not matter much, as the gases were afterwards treated in vitriol-chambers. But already then it was noticed that the gas containing 4 per cent. SO_2, if sent through a second contact-furnace, came down to 0·2 per cent. SO_2, so that in all 97 per cent. was converted into SO_3. In 1889 it was

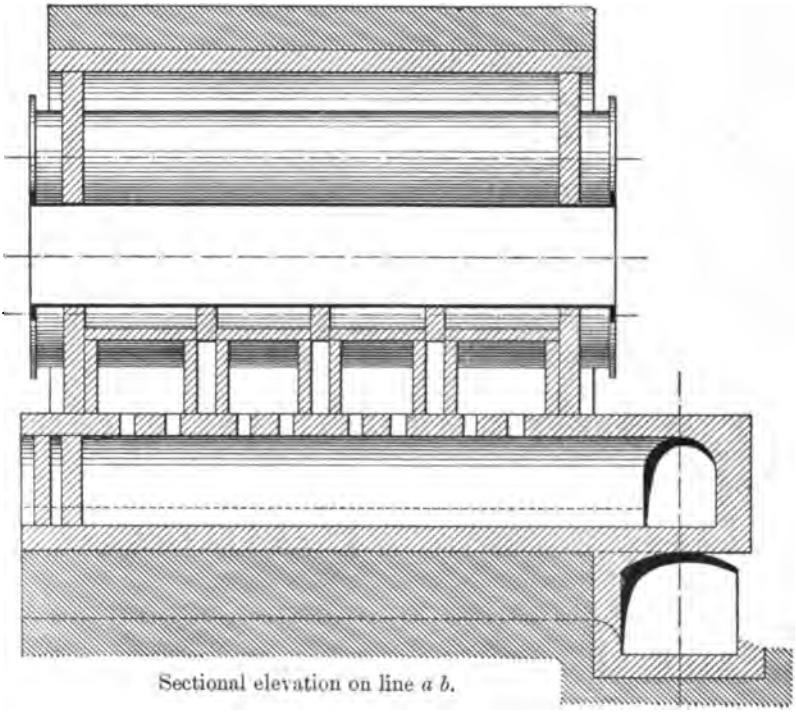
Fig. 468.



noticed that the formation of SO_3 was increased to 85 or 90 per cent. by one single passage through the contact-substance, if the percentage of oxygen essentially exceeded that of sulphur dioxide; since then gases with only 6 per cent. SO_2 have been worked and the uncombined residue of SO_2 is removed by absorption.

7. *The contact-furnace.*—The sketches, figs. 468 & 469, show that each furnace contains five horizontal retorts, charged with contact-substance and heated by means of a gas-producer. Such a furnace yields from 20 to 24 cwt. SO_3 per 24 hours.

Fig. 469.



Sectional elevation on line *a b*.

8. *The absorption of the anhydride.*—The SO_3 vapours, escaping from the contact-retorts under slight pressure, are completely absorbed in vertical towers fed with concentrated sulphuric acid, the acid flowing out strongly fuming. It is either sold in this state or is worked for anhydride by distillation in iron retorts.

VI. *Rabe's Process.*

Concerning Rabe's process for the manufacture of sulphuric anhydride I have received the following communications through Mr. Niedenführ, who has erected several plants on this system, which performs three operations—the purification of the gases, the contact-process, and the absorption of the SO_3 formed. The purification is described in a Hungarian patent No. 22,959, of Nov. 12, 1901. The misty particles contained in the gases must be removed so completely that even after a number of years no deposit is formed on the glass windows interposed in the pipes, and of gaseous admixtures only those must be left which are absolutely harmless.

The hot gases are cooled by direct contact with the cooling-liquid, in two phases. In the first the cooling-effect is carried on up to the point that the liquid completely evaporates; in the second phase so far that the liquid is only heated. This admits of carrying out the cooling-process in a vessel made of an unalterable material, *e.g.* pottery surrounded on the outside by lead or iron. Such apparatus is not acted upon or stopped up even if the sulphuric acid used for drying has a concentration of 60° B.

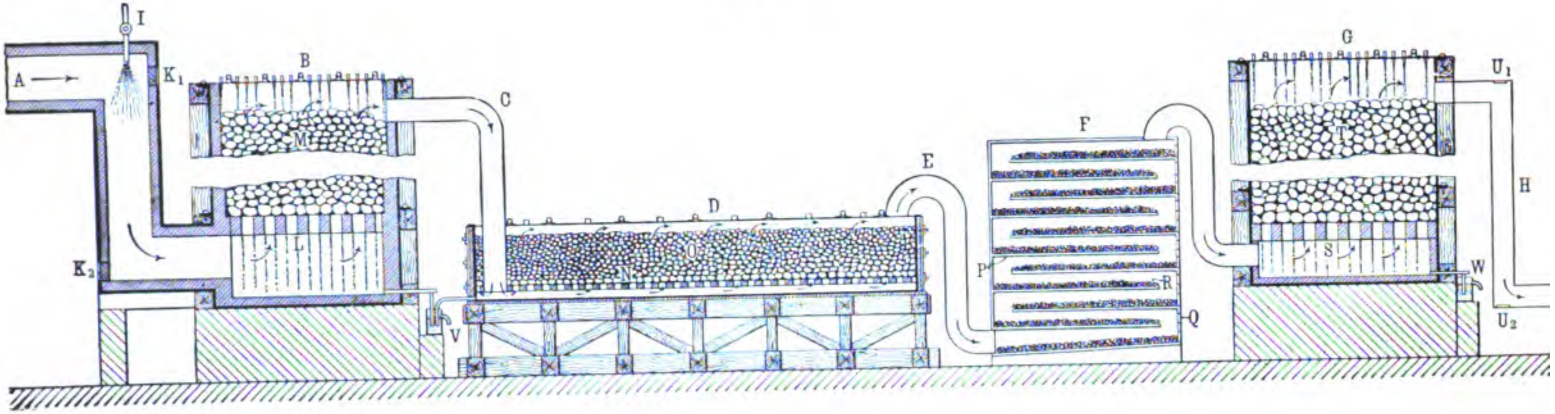
The purifying process will be better understood by means of the sketch (fig. 470).

The gas enters by a cast-iron pipe A, lined with acid-proof material and possessing cleaning-holes K_1 and K_2. By means of the Körting's spray-producer I enough water or sulphuric acid is introduced to be completely evaporated. The cooling of the gases thus effected is completed by tower B. This is built like a Glover tower, the bottom and sides being lined with acid-proof pottery; by the grid L the packing M is supported and is moistened by cold strong sulphuric acid, fed in at the top and equally distributed. The hot acid is run out by V into a cooler. The mud is easily collected and no stoppage of the tower takes place.

The cooled gases are now freed from mechanically suspended impurities by filters, consisting of a lead box D, in which on a grid N the filtering-material O is spread in a thin layer. The latter consists of small pieces of coke, from 10 to 1 mm. diameter, systematically placed so that the coarser grains are at the bottom, the finer at the top. The filtering surface must be very considerable in order to avoid loss of draught by friction. The impurities collecting in the filter are removed from time to time by rinsing.

In lieu of the finest grain of coke, fibrous materials may be

Fig. 470.



employed, *e.g.* asbestos, which is prevented from being compressed by being spread on several sieves adjoining each other.

By the filtering-processes the gases are rendered absolutely transparent, which is constantly controlled by means of glass sights; but they still contain gaseous impurities. Only the constituents of atmospheric air — oxygen, nitrogen, carbon dioxide, argon, &c.—are harmless; all other gases (besides SO_2) must be removed. Rabe has found that hydrogen chloride occurs in roasting-gases, and that it can be removed by sodium bisulphate in concentrated solution or in pieces. This takes place in box F, with shelves P and purifying-material R.

The gases are now dried in the acid-fed tower G, containing a packing T on grid S, and pass through pipe H, provided with glass-sights U_1 and U_2, into the contact-apparatus (not shown !). W is the hydraulic seal for the acid running out of G.

Rabe considers as special advantages of his purifying-process: the possibility of working with natural draught, the complete drying of the gases, the removal of the misty particles without the use of a washing-process, and therefore but slight expense for maintenance and supervision.

(The same advantages are claimed by Rabe for producing acid free from iron and arsenic when made by the lead-chamber process, in lieu of acid made from brimstone.)

Concerning the contact-process itself, Dr. Rabe gives me the following notes:—The purified and dried gases are brought into contact with the catalyzer in comparatively wide chambers, where the mass is spread on sieves, between which loose sieves can be interposed. This arrangement is preferable to placing the contact-mass in narrow tubes, as the mass can thus be spread more uniformly, which can be controlled at sight, and as the gases are always mixed over again after having passed through a layer of contact-substance, so that any inequalities in the temperature and composition are removed. It is also possible by this means to carry out the reaction in different phases, by employing different contact-masses, or different temperatures, or combinations of both. In order to produce the proper temperatures, various means can be employed. Thus, according to the German patent application R 13,221, "regulating"-tubes can be placed in the contact-chamber, or as bearers for the contact-sieves, which communicate their temperature to the contact-mass. Wide contact-chambers also produce the least resistance to the propulsion of the gases.

The degree of conversion of SO_2 into SO_3 is most easily calculated from the analysis of the gases before entering and after leaving the contact by Reich's method (p. 411). If, for instance, 10 c.c. decinormal iodine solution is employed for each test, corresponding to about 12 c.c. gaseous SO_2 at ordinary temperatures, and if before entering the chamber the water run out of the aspirator had been=150 c.c., but after leaving the chamber= 3000 c.c., the degree of conversion is:

$$\frac{(3000-150)\,100}{3000-6}=95{\cdot}2 \text{ per cent.}$$

If for the second test another quantity of iodine solution had been used, a corresponding correction must be made.

In order to properly absorb the SO_3 by concentrated sulphuric acid, the latter must be kept cool, which Rabe effects by specially constructed "reaction-towers" with surface-feeding.

In Zsch. angew. Ch. 1900, p. 960, Niedenführ mentions that the total fuel required for producing 100 parts SO_3 is 20 kg. coal. The supervision of the process is very simple, and is facilitated by automatic apparatus on the principle of Rabe's measuring-process for gases and liquids (G. P. 111,019 and 112,835).

The B. P. of Rabe, No. 3327, 1901, substantially agrees with the preceding description, but we shall quote the claims verbatim. The hot gases are preliminarily cooled in conduits with neutral walls, by means of vaporizing water or sulphuric acid, to a temperature at which there is not yet condensation of fluid matters, then cooled to a temperature of less than 100° C., by direct contact with sulphuric acid of any preferred strength in towers of not too close packing, and conducted systematically through filtering-layers of granular substance gradually reduced in size, or of fibrous character, until, when in a dry state, they leave no efflorescence on the glass of the Tyndall testing-apparatus even after a long time, and then, after being entirely freed from any non-neutral gaseous elements by means of suitable reagents (as, for instance, from muriatic acid by means of bisulphites in a solid form or in the form of a concentrated solution), are dried in the usual manner.

Dr. Rabe informs me that his process has already been introduced for manufacturing sulphuric anhydride from pyrites lumps and fines and from zinc-blende. The following results have been obtained at one of these places during a prolonged period of work. Cost of 100 kils. sulphuric anhydride:

	Mark.
96 kils. pyrites 43 per cent. S at 1·80 Marks	1·73
10 ,, coals at 2 M.	0·20
2·4 H.P. hours for moving gases and acid at 0·05 M. per electrical H.P.	0·12
0·16 shift at 2·50 M. per man and shift	0·40
Repairs	0·32
	2·77
Sinking fund for plant, costing 130,000 Marks per 5000 kils. per day, equal per 100 kg. to	0·87
Total............	3·64

(The amount of 130,000 Marks for a daily production of 5000 kils. SO_3 does not include royalty, and is decidedly less than will be required in most places for a substantially constructed plant.—G. L.)

RECENT PROPOSALS FOR IMPROVING THE MANUFACTURE OF SULPHURIC ACID BY THE CONTACT-PROCESS.

None of the following proposals seem to have been as yet introduced into manufacturing practice, except Winkler's improved platinum asbestos, which has been recently superseded even at the Freiberg works (p. 1076). These proposals must, however, be enumerated for the sake of completeness.

A. *Purification of the Gases.*

The problem of purifying the pyrites-burner gases from flue-dust is fully discussed in the communications from Freiberg, from the Badische, from Rabe, &c. We mention here the proposal of Raynaud and Pierron (Engl. pat. 16,283, of Feb. 15, 1900) to effect this end, first by condensing or compressing the gases and then allowing expansion to occur. They prefer condensing the gases by absorbing them in Kieselguhr, and expanding them by raising the temperature after a certain interval. The impurities are said to remain behind in the porous material, which must be from time to time renewed.

G. C. Stone (American patents Nos. 711,187 and 711,188, of Oct. 14, 1902) removes the arsenic vapours from burner-gases by cooling the gases down to a temperature at which the arsenic condenses, retaining the latter in a filtering-medium. The latter is afterwards freed from arsenic by heating, and the arsenic is condensed.

B. *Contact-Apparatus.*

Remmert (G. P. 59,556, of Dec. 23, 1890) laid down the principle that when hot gases are passed over solid substances whereby they undergo a change with development of heat, layers of different temperature are produced at right angles to the direction of the gaseous current. This holds good also in the formation of SO_3 by the contact-process. The gases, getting heated by this process, raise the temperature of the following layers of the contact-substance to the point of reaction. Thus the reaction spreads over the whole mass, but the heat of the gases going out is lost. This can be avoided by reversing the direction of the gaseous current, when the heat is at a maximum at the far end of the contact-apparatus, and introducing the gases first at that end. This causes a more equal temperature and a saving of fuel in the previous heating of the gases.

Raynaud and Pierron (Engl. pat. 16,254, of Feb. 15, 1900) improve the catalytic action in one of the following ways:—1st, the temperature is kept uniform, but the contact-substance used is first poor in platinum, then rich, and then again poor; 2nd, the contact-substance remains the same, but the temperature is first low, then higher, then again lower. During the first phase the reaction SO_2+O is commenced, during the second phase it is completed, but as there is again a dissociation of SO_3, this is brought back in the third phase.

Babatz (Engl. pat. 1216, of Jan. 19, 1900) heats the purified kiln-gas by the non-purified gases on their way to the purifying-plant. The heat obtainable from this source should be more than sufficient for bringing up the purified gases to such a temperature that no further heating of the contact-apparatus is required (comp. *suprà* the previous patents of the Badische and of Höchst).

Daub and Deuther (B. P.9536, of April 24, 1902) try to prevent the over-heating of the contact-substance by the reaction-heat in the following manner:—The apparatus consists of alternately arranged heating- and contact-chambers, the former being provided with independent means for heating or cooling the gases, and the latter with a passage for the whole of the gas conducted into the apparatus through contact-material disposed in the contact-chamber in such a manner that the gases and contact-matter reciprocally maintain and equalize the temperature in the chamber and prevent local overheating.

P. Naef has taken a number of patents concerning a method of treating solid materials with gases, consisting in passing hot gases through the solid material, withdrawing, readjusting the temperature, and repassing the gas through the solid material so as to simultaneously produce several gas-circuits through the solid material. In one of these (B. P. No. 23,415 C, April 26, 1899) he brings in the oxidation of HCl or SO_2 by air. Other patents follow in 1900, No. 18,188 with 134 claims, No. 18,191 with 154 claims; then No. 14,977 of 1901.

The Tentelewsche chemische Fabrik (French patent, 321,275, May 20, 1902) describe various modifications for regulating the temperature in the contact-oven.

Wenmaekers (B. P. 19,902, of Oct. 15, 1901) passes the gases from pyrites-kilns through cooling-pipes, then through a dry coke-tower, thence to another tower into which steam is injected, and lastly through a coke-tower sprayed with concentrated sulphuric acid. From here they pass into the contact-apparatus, the heat of the issuing gases serving to heat up the arriving gases. After taking out the sulphuric anhydride formed, the gases, still retaining SO_2, are returned to the steaming-column and re-enter the process.

Stone (U.S. P. 711,186, of Oct. 14, 1902) describes a contact-apparatus consisting of independent sections, each containing an individual charge of contact-substance. Each section, as its charge becomes spent in working, is replaced by a freshly-charged section.

Herreshoff (U.S. P. 719,332 and 719,333, Jan. 27, 1903) effects a partial conversion of the gases into SO_3, then cools the residual gases by heat exchange with entering gases, and returns them to the contact-apparatus for complete transformation For this he employs a specially constructed apparatus.

H. A. Frasch (U.S. P. 715,778, of Dec. 16, 1902) obtains sulphur dioxide in a concentrated condition, suitable for the manufacture of sulphuric acid or anhydride by the contact-process, as follows :—The pyrites-burner gases are washed and cooled and subjected to pressure in contact with water already saturated with SO_2 at atmospheric pressure; they are then washed under pressure with fresh water, and the surcharged solution is reduced to atmospheric pressure, the gas evolved being stored or at once utilized. The surplus solution is heated, and the SO_2 evolved is returned to the absorber.

Ferguson (B. P. 6824, of March 24, 1903; U.S. P. 723,595 and 723,596, of March 3, 1903) employs two contact-chambers; after the gases have passed the first, and have been partially converted into SO_3, more air is mixed with these, and they are now passed through the second chamber, where the conversion is completed.

Sébillot (E. P. 21,616, of Oct. 14, 1898; U.S. P. 700,249, of May 20, 1902) makes sulphuric acid (*not* anhydride) by burning sulphur-ores in a "blast-furnace" in which ore and fuel are alternately charged, air being forced in. The gases pass into a mixing-chamber, and from this into contact-chambers. These contain, on a perforated bottom, pieces of pumice-stone, the interstices being filled with loose asbestos, and above this a series of perforated stoneware plates, each supporting a layer of asbestos and of spongy platinum. Into the free space above, the hot mixture of sulphur dioxide and air is led along with steam and a regulated supply of air, and the gaseous mixture is drawn down through the contact-material into the bottom chamber of the column, in which pipes are set, cooled by a current of water, whereby the acid-vapours are condensed.

Le Blanc and Krauss (U.S. P. 726,076, of April 21, 1903) pass gases, containing about 7 per cent. SO_2 and 9 per cent. O, into a first contact-chamber, kept at about 500° C., in the proportion of about 120 litres of burner-gas to 1 kilog. platinized asbestos per minute, and afterwards at the same speed through a second chamber kept at about 400° C.

C. *Absorbing-Apparatus.*

Stone (U.S. P. 695,180; Journ. Soc. Chem. Ind. 1902, p. 476) describes an apparatus for cooling and absorbing sulphuric anhydride, composed of a number of pipes and presenting no special interest.

According to the Alkali Inspector's Report, No. 38, p. 16, similar difficulties in completely retaining the white fumes as have been observed in the case of top-fired pans (p. 816) have been also met with in the manufacture of SO_3 by the contact-process.

For the absorption of SO_3 we must take into account the considerable quantities of water introduced into the process by the operations of washing and drying. These are converted into dilute acid, and must be brought up to H_2SO_4 by means of SO_3. In the Ludwigshafen process the quantity of SO_3 and SO_2 taken out of the gases by the washing-operation is from 6 to 8 per cent. of the total. Much more is taken up by the operation of drying the gas. With gases of 7 volume per cent. SO_2 the weight of SO_3 per cubic metre is 250 grams. If the gases leave the washers at 25° C., saturated with moisture, they will contain per cubic metre (at a tension of 23·5 millim.) 27·3 grams H_2O, corresponding to 121·3 grams SO_3, or nearly half of the above 250 grams. Altogether about 60 per cent. of the SO_3 formed is converted by water into H_2SO_4, leaving 40 per cent. at disposal in the free state.

Herreshoff (U.S. P. 722,981, of March 17, 1903) passes into a vessel, provided with a cooling-jacket close to its bottom, the vapours of SO_3, and at the same time enough water or dilute acid to produce an acid of the desired strength.

D. *Improvements in the Manufacture of Contact-Substances.*

It may be assumed that one kilogram platinum, in the shape of ordinary platinum asbestos, can produce with a good process from 600 to 700 kilograms SO_3 per 24 hours. The high price of platinum makes it desirable to prepare very active contact-substances.

A German patent of Cl. Winkler's (No. 4566, Sept. 21, 1878 describes the preparation of extremely active catalytical substances from precious metals or metallic oxides in the finest state of division, with which an indifferent porous matter is impregnated almost in the same way as a textile fabric is dyed in the bed. The best catalytical substance is platinum, also iridium or palladium, less so the oxides of iron, chromium, manganese, cobalt, and copper. As an indifferent menstruum almost any loose porous substance may be used, preferably asbestos, but also glass-wool, pumice, infusorial earth (Kieselguhr), clay, and where a very high temperature is not required, even cellulose, cotton-wool, guncotton, sponges, &c.

In order to charge asbestos with finely divided platinum, it is thoroughly soaked with a solution of platinum chloride made alkaline by soda and mixed with sufficient sodium formiate to reduce the platinum. The well-wrought pasty mixture is dried in a water-bath; thus the platinum is separated as "platinum black," and is firmly precipitated upon the fibre. The salts are removed by washing, without washing off the platinum. The quantity of the latter precipitated depends upon the strength of the solution of platinum chlorides ; with asbestos or cotton-wool a percentage of 80 platinum may be attained. Metallic oxides exhibit catalytical action only at higher temperatures, and, accordingly, must be precipitated upon fire-proof substances. Thus asbestos or pumice may be thoroughly impregnated with chromium oxide by soaking in mercurous nitrate, then in ammonium chromate, drying each time, and ultimately gently igniting. Cupric oxide is precipitated firmly by soaking in an ammoniacal solution of cupric carbonate and gently igniting. Asbestos may also be soaked with solutions of manganous or cobaltous chloride, &c., dried, put into a heated solution of bleaching-powder or of another precipitant, dried again, washed, and ignited. The contact-substances prepared in this way, owing to their homogeneous condition and their very large surface, cause, either at the ordinary or at a higher temperature, the combination of certain gases, such as that of SO_2 and O into SO_3, the conversion of the CS_2 in coal-gas into H_2S, the oxidation of the vapour of alcohol, &c. They may be employed for all reactions based upon the phenomena of so-called "catalytic action."

The preparation of extremely active platinum black has been described by Loew (Ber. d. deutsch. chem. Ges. 1890, p. 289). Already Doebereiner has shown that the degree of activity of platinum black differs very much with the method of preparation employed. That made with zinc and hydrochloric acid is less active than that made with an alkaline solution of glucose, and this is inferior to that which is precipitated from platinic sulphate by alcohol. The proportion is 1 : 1·8 : 2·6. Far more active again is the following preparation, made with formaldehyde of 40 or 45 per cent. :—50 grms. platinic chloride are dissolved in a little water, to a volume of 50 or 60 c.c., and mixed with 70 c.c. of 40 to 45 per cent. formaldehyde. To this is added, quite gradually and with good cooling, a solution of 50 grms. caustic soda in the same quantity of water. Most of the metal is separated at once. When, after 12 hours, the mass is filtered by means of a filter-pump, a yellow solution passes through, which on boiling separates a little metal. When, however, most of the salts (sodium chloride and formiate) has been removed by washing, a deeply black solution runs off, some of the black mud going into solution. Therefore the washing is interrupted until an oxidizing process now going on in the black mud has been finished, whereupon the liquor runs off colourless. That process consists in the rapid absorption of oxygen by the black mass on the filter; the temperature rises to 36° or 40°, and many gas-bubbles are given off with a crackling noise, lasting for several hours. The fine mud has now turned into a loose porous mass, which is washed till every trace of chlorides has been removed, then pressed and dried over sulphuric acid. Even a trace of sodium chloride is extremely prejudicial to the action of the platinum black, a coating of platinous chloride being formed in that case. The black mass evidently contains an organic compound of platinum, which is afterwards destroyed by oxidation.

Majert (G. P. 134,928) dissolves platinum chloride in ethyl alcohol, methyl alcohol, acetone or acetic ether, soaks asbestos or the like in that solution, and sets fire to it. The platinum is reduced to the metallic form in a very fine state of division, and firmly attached to the asbestos. Thus platinized asbestos of great efficacy can be obtained with only 2 per cent. platinum.

Langhans (G. P. 134,738) employs the double compounds of methyl sulphide or its homologues with the halogen compounds of platinum dissolved in bromoform.

Klaudy and Efrem (E. P. 14,339, of 1899) employ as usual a fire-proof carrier, with a platinum salt and an organic reducing-substance, but together with hydrofluoric or hydrofluosilicic acid. They employ meerschaum or clay, which is treated with aqua regia or strong sulphuric acid, and freed from the soluble salts thus formed by washing with water. They then add the platinum salt and a reducing-agent, such as sugar, with or without finely divided carbon, and, moreover, hydrofluoric or (preferably) hydrofluosilicic acid, the latter for the purpose of forming a hard porous mass, which especially acts also by etching the smallest particles of the clay and enlarging the active surfaces. The paste thus formed is moulded, dried, and ignited. These masses act as catalyzers already at ordinary temperatures, especially for lighting gas-flames, and are much harder and more durable than platinized asbestos, &c.

Goldenberg, Geromont, & Co. (E. P. 618, of 1900) prepare contact-substances from non-porous sintered materials in the shape of spheres, cylinders, or plates, on which a very thin porous layer of clay has been fixed by burning. Both materials must be heat- and acid-resisting. These bodies are treated with platinum solution, which penetrates only the porous surface, leaving the sintered cores free, so that the platinum is fully utilized by the gases circulating between the bodies which diffuse through the thin layer.

Saubermann (G. P. 125,988) divides the asbestos into fine parallel fibres, which are spun into tissues (principally for incandescent mantels).

C. J. E. de Haën (B. P. 8545, 1901; U.S. P. 687,834) mixes asbestos with *vanadic acid* in a fine state of division by soaking it with ammonium vanadate and igniting. This reagent is asserted to effect a combination of SO_2 with O up to 84 per cent. at a temperature of 465° C. Haeussermann (Chem. Zeit. 1902, p. 6) points out that the vanadium compounds have been known for a long time as oxygen carriers, and have also been proposed for the present case.

Bonhard and Loyer (F. P. 321,573, April 22, 1902) employ the oxides of metals of the *tantalum* group, after reducing them in the electric furnace to a spongy mass, as a contact-material for the manufacture of SO_3.

According to the French patent, No. 318,770, of the Comp. Parisienne de Couleurs d'Aniline, asbestos soaked in *phosphoric acid* and dried transforms 90 per cent. of SO_2 into SO_3.

Neuendorf (G. P. 127,846, Oct. 28, 1899) evaporates a solution of barium (strontium or calcium) chloride to dryness, impregnates the dry crusts formed with a solution of platinum chloride, dries the mass, and converts it into sulphate by a stream of SO_2, steam, and air, or by vapours of H_2SO_4 at a high temperature. Or, preferably, he first forms the sulphate in the aforesaid manner, and subsequently soaks it with platinum chloride.

Porter (U.S. P. 612,614, of Oct. 18, 1898) describes (principally for use in lighting gas-jets) mixtures of a catalytical metal (platinum, &c.) with infusible metallic oxides (mainly Al_2O_3, but also the oxides of Zr, Ce, Mg, &c.) produced as follows:—A solution of 1 part platinum chloride is mixed with 8 parts hydrated aluminium chloride and the mixture is used for impregnating cotton, wood-pulp, or other combustible materials. This product is heated in contact with air, the organic substance is burnt and leaves behind a mixture of metallic platinum and alumina in a very porous form. The organic substance causes the reduction of Pt at a low temperature and the alumina prevents the platinum black from uniting into a denser form. Preferably 1 part Pt is employed to 2–6 parts Al.

Briegleb (G. P. 121,906, of Jan. 25, 1900; B. P. 11,792, of June 18, 1901) moulds the oxides of iron, copper, or chromium with 10 per cent. clay into briquettes, places them on a grate in an upright shaft, and heats them by means of a second, lower grate, on which coke, anthracite, or charcoal, free from hydrogen, are burnt, or else by producer-gas. The fuel must be free from hydrogen. [Such a fuel, whether solid, liquid, or gaseous, is not known, nor is the heating of the contact-substance at all necessary, as the heat of the burner-gas is quite sufficient for this purpose.]

Blackmore (U.S. P. 686,021, of 1901) passes hot sulphur dioxide, containing vapours of sulphur, over ferric oxide in order to produce SO_3, on the principle of replacing the oxygen of ferric oxide by a substance possessing greater affinity to the metal [?].

The same (U.S. P. 686,022) brings SO_2 into contact with Fe_2O_3 at a temperature lying below the dissociation point of SO_3, passes the SO_3 formed into a condensing-apparatus, raises the temperature of the iron residue, passes oxygen over it, allows to cool down to a suitable point, and recommences the operation by admitting SO_2.

Hans A. Frasch (U.S. P. 664,634, of Dec. 25, 1900) passes the gases from ordinary ore-burners into a "converter" in which some more sulphur-ore (preferably pyrites) is contained, but only enough ore is burned therein to maintain the proper temperature and to produce fresh ferric oxide. The gases pass through this catalytic converter from the top downward; there may be a magazine provided for self-feeding, so that the amount of cinder drawn from the bottom regulates the charge of fresh ore and hence the temperature. If necessary, the gases coming from the ordinary roasting-furnace (pyrites-kiln, &c.) can be cooled before entering the catalytic converter, the temperature of the contact-mass being regulated by adjusting the proportions of sulphur burning in, and the SO_2 gases admitted to, the converter. Such a catalytic converter, burning a moderate quantity of pyrites, may be added to the ordinary burners used in the metallurgy of zinc, copper, nickel, &c.

Carey, Heslop, and the United Alkali Co. (B. P. 10,351, of 1902) precipitate platinum upon inorganic salts (sulphate of soda). In this case any acid and aqueous particles contained in the gases are said to do no harm.

Hoelbling and Ditz (G. P. 142,144, of April 9, 1902) employ rare earths : Ce, La, Di, Th, Y.

Masson (Fr. P. 324,859) produces HCl, together with SO_4H_2 or SO_3, by heating equivalent quantities of Cl, SO_2, and superheated steam, with or without the presence of platinum asbestos.

E. *Manufacture of SO_3 from By-products.*

Acid-tar, as obtained in the chemical treatment of petroleum, paraffin, and the like, is utilized for the manufacture of SO_3 by J. D. Starck (E.P. 12,028, of Aug. 29, 1889) in the following manner :—The acid-waste is fed in at the lower end of an inclined iron retort, within which revolves an endless screw, for the purpose of drawing outwards the residual coke-like mass. The sulphur dioxide and water produced are freed from water and hydrocarbons by means of a condenser and wash-chamber; they are then dried in a sulphuric-acid tower, mixed with a suitable proportion of dry air or oxygen, and conducted through a tube containing platinized asbestos or other contact-substance. The SO_3 produced is condensed or absorbed in sulphuric acid, and the residual SO_2 is passed into ordinary vitriol-chambers.

Recovery of sulphuric anhydride from waste materials containing such, as obtained in the manufacture of coal-tar colours.—This is the object of a proposal of Schulze-Berge (G. P. 35,620), who employs a partial vacuum for distilling SO_3 from such mixtures by means of a special apparatus. Already in 1885, Aug. 8th, E. D. Kendall (U.S. P. 323,583) prescribes the distillation in a partial vacuum for recovering the SO_3 from a mixture of fuming sulphuric acid with organic substances, in order to lower the temperature and to produce less SO_2.

Carey, Heslop, and the United Alkali Co. (E. P. 10,317, of June 5, 1900) treat the *waste gases from the Claus-Chance process* for the recovery of alkali-waste in the following manner :—The gases are passed with air through a furnace to burn the H_2S into SO_2, then dried in a tower by sulphuric acid, and then passed over or through a catalytic agent, such as platinized asbestos or iron oxide, maintained at a suitable temperature, to obtain SO_3. According to the Alkali Inspector's Reports, No. 38, p. 15, this process was successful on the small scale, but was found too expensive to be introduced into actual practice.

CHAPTER XII.

OTHER PROCESSES FOR MANUFACTURING SULPHURIC ACID.

ALL the other processes which have been proposed for producing sulphuric acid, numerous as they are, can be dismissed with a very few words, since not one of them has had any technical success or promises to become successful in the future, except perhaps the first. The details can be found in the places quoted.

I. *Oxidation of Sulphurous Acid by means of Nitrous Acid, but without Lead Chambers.*

Proposals for replacing the lead chambers by chambers made of india-rubber, gutta-percha, slate, "zeiodelite," glass, &c. have been mentioned on p. 422.

MacDougal and Rawson (patent of Nov. 21st, 1848) conduct sulphur dioxide and air through nitric acid contained in a Woulfe's bottle, in which sulphuric acid and nitrogen peroxide are generated; the latter, with the air in excess, passes through several vessels filled with water, in which the nitric acid is regenerated.

Hunt (patent of Aug. 16th, 1853) conveys a mixture of sulphur dioxide and air through a tower filled with pebbles, in which nitrous vitriol continuously trickles down. This principle had already been proposed by Gay-Lussac; and it is actually carried out in the Glover towers, so far as it is practicable—that is, by conducting the escaping gases into lead chambers. (Comp. also pp. 979 and 980.)

Persoz ('Technologiste,' xvii. p. 461; 'Dingler's Journal,' cxxxix. p. 427; Wagner's 'Jahresbericht,' 1856, p. 54) passes sulphur dioxide through nitric acid diluted with from 4 to 6 volumes of water, and heated to 100° C., or through a mixture of nitric acid or a nitrate with hydrochloric acid, in a comparatively small glass or stoneware vessel, promoting contact by an agitator.

The gases generated by the reduction of the nitric acid ascend in condensing-towers, where they are regenerated into nitric acid by an ascending current of air and a descending jet of water. The sulphur dioxide might even be diluted with carbonic acid, nitrogen, or other gases. In theory this process is right enough; in practice it is said to have failed, principally from the difficulty of constructing vessels suitable for resisting the acids (?).

Verstraet's tubular apparatus (' Bulletin de la Société d'Encouragement,' 1865, p. 531; 'Dingler's Journal,' clxxix. p. 63; Wagner's ' Jahresbericht,' 1865, p. 226) has been mentioned previously (p. 476). The Jury Report of 1851 asserted that similar stoneware vessels, constructed by Fouché-Lepelletier, were at work at Javel, near Paris, and that in that factory one-third of the annual make of 3600 tons was produced in them, with one-third of the cubic contents and at one-eighth of the cost of lead chambers. This assertion has been proved to be entirely erroneous by original correspondence in Hofmann's ' Report by the Juries,' 1862, p. 8.

Lardani's apparatus (Bull. Soc. Chim. viii. p. 295; Chem. News, 1868, No. 441, p. 238) has also been described above (p. 476); it exemplifies no essentially novel principle.

Kuhlmann (English patent, Dec. 11, 1850) proposed to force a mixture of sulphuretted hydrogen (from soda-waste) and air through nitric acid, by which nearly all the sulphur was said to be oxidized to sulphuric acid; this is, however, not the case.

Petrie (English patent, Aug. 11, 1860) employs a system of stoneware pipes filled with pebbles, through which a current of nitric acid passes from one side, and one of SO_2 and air from the other, the quantities of the materials and the construction of the apparatus being arranged in such a manner as to avoid any loss of nitric acid.

Finch and W. J. & S. Willoughby (E. P. 3086, 1884) pump a mixture of burner-gases, nitrous fumes, and steam into a tower, where they are subjected to a certain amount of pressure, in order to facilitate their combination. The escaping gases pass forward into other similar towers, and at last through a Gay-Lussac column.

W. Burns (E. P. 14,441, 1886) seeks also to promote the combination of the gases by pressure, together with a peculiar kind of agitation, in an ingeniously devised, but hardly practicable apparatus.

Hannay (E. P. 12,247, 1886) passes the sulphurous and nitrous gases through a condensing-tower, where they become minutely subdivided and thoroughly mixed by passing through screens, which are kept moistened by a continual stream of water trickling on them, the process being repeated until the solution of sulphuric acid formed acquires sufficient strength, when it is drawn off and a fresh supply of water is run into the apparatus.

A. & L. Q. Brin (E. P. 12,070, 1886) burn pyrites with pure oxygen, and convert the mixture of SO_2 and O into sulphuric acid by means of nitrous fumes. A special apparatus for this purpose is contained in my own patent No. 3166 of 1888, which, however, was only taken to cover the ground, the principal object of my invention being the production of sulphuric anhydride, for which the cost of pure oxygen might be more easily afforded than for ordinary sulphuric acid. That oxygen cannot be prepared, as some imagine, in a cheap way by electrolysis, employing the hydrogen evolved as fuel for dynamo-machines, has been demonstrated by Scheurer-Kestner, in criticising a proposal of Justinus Mullerus for manufacturing sulphuric acid without chambers by means of oxogen obtained in the above manner (Bull. Soc. Ind. Mulh. 1890, p. 276). 1 kilog. of oxygen (100 litres at 0° and 760 millim.) per hour would require a dynamo of 12½ horse-power, or 131,250 calories, which means burning about 18¼ kilog. of coal, which in France cost about 3½*d.*; the corresponding amount of hydrogen by its combustion would only furnish 4312 calories, or 3 per cent. of the above. A ton of real H_2SO_4 requires 490 kilog. oxygen, which would cost £7 3*s.*!

Durand, Hugnenin, & Co. (F. P. 205,589, May 9, 1890) pass a mixture of sulphur dioxide and air through tanks, charged with nitric acid or solutions of nitrous products, alternating with condensing-towers. The liquids are made to flow systematically through the apparatus in such a manner that at last concentrated sulphuric acid, free from nitric or nitrous acid, is obtained. The above-mentioned gaseous mixture is produced by passing compressed air into sulphur- or pyrites-burners, thus also obtaining the pressure necessary for forcing the gas through the liquids contained in the tanks.

Barbier's apparatus for manufacturing sulphuric acid (B. P. 12,726, 1892) consists of six towers, arranged in steps, packed with hollow pieces of sandstone, quarts, or the like. Burner-gas enters the bottom tower and passes through them all. The towers are connected alternately at top and bottom; the last serves as a Gay-Lussac. Nitrous vapours and steam are introduced from a concentrating-pan fired from without. The acid formed in the towers drops into concentrating-pans placed below their open bottoms, or into a collecting-vessel. They are fed with a mixture of sulphuric and nitric acid, if necessary also with steam. Private reports concerning Barbier's apparatus complain of an excessive consumption of nitric acid and also obstructions. The high royalty also acted as a check upon experiments with it. Candiani (Chem. Ind. 1895, p. 153) remarks that the only Italian factory which had introduced Barbier's process (Villafranca) had not been very successful with it. Boissieu (Bull. Soc. Chim. (3) xi. p. 726) asserts that the Barbier system has answered very well, but he unfortunately does not quote any figures or other proofs for this assertion; Pierron (Mon. Scient. 1900, p. 367) reports authentically that it has been entirely abandoned.

Staub (Engl. pat. 12,675, 1894) describes a set of five towers, packed with specially moulded earthenware pieces, and fed with nitric acid, nitrous vitriol, &c. Staub's apparatus does not differ in any essential point from the principle of making sulphuric acid by towers alone, without lead chambers, as attempted by a number of inventors before him. His strange contention that he was entitled to a patent for that *principle*, because he had been the first to carry it out by a special apparatus, was rejected by the German Imperial Court and his German patent No. 88,784 cancelled. Moreover the apparatus which he had set up in 1895 at Stolberg and in 1896 at Wittenberg was worked only during a very short time and then stopped on account of bad results and of extremely high consumption of nitre.

I have already (p. 501) expressed the opinion that *theory* does not at all prevent the assumption of the possibility of making sulphuric acid in towers alone, without vitriol-chambers, on a commercial scale. We have also seen (p. 493) how Mr. Niedenführ plans a system working with towers alone. It is quite possible that this may ultimately fulfil its purpose, but it would of course require a good deal of trouble till all details are worked out, and especially till that drawback is removed which has frustrated all former efforts in this direction, viz., the excessive consumption of nitre.

II. *Processes dispensing with Nitre.*

Gossage (patent of Oct. 6th, 1857) burns sulphuretted hydrogen from soda-waste, cools the products of combustion, allows them to ascend in a coke-tower fed with water, runs the solution of sulphurous acid thus obtained down another coke-tower supplied with hot air, by which the SO_2 is partly changed into SO_4H_2, and conveys the remaining SO_2 into a lead chamber, where it is completely oxidized in the usual way. According to Gossage's own avowal (Hofmann, Report by the Juries, 1862, p. 9) this process is not practicable.

Petrie (patent of Nov. 1st, 1852) allows a mixture of sulphur dioxide and water, heated to 300°, to meet a spray of water in pipes of earthenware or iron filled with silica, or finely divided platinum, &c.

Hähner (patent of March 28, 1854) employs chlorine in the presence of aqueous vapour for oxidizing SO_2. The same process has been patented by Macfarlane (Jan. 14, 1863).

Houzé proposes (Monit. Industr. vii. p. 65) to bring sulphur dioxide, air, and steam into contact in stoneware vessels at a temperature a little below red-heat. Similar vessels are said to permit distilling the acid by means of heated air or superheated steam without any bumping.

Surcouf (Fr. P. 310,600, May 7, 1901) manufactures sulphuric acid from sulphur dioxide (and nitric oxide from ammonia) by means of ozone, heating the apparatus from the outside by steam or hot gases, in order to hasten the reaction.

Deacon showed in 1871 (Chem. Trade J. 1889, vol. v. p. 193 that a mixture of SO_2 and atmospheric air in the presence of a solution of cupric sulphate is converted into sulphuric acid, but this seems to have become very little known. Later on the same invention was made by Roessler, and was specially applied to the absorption of acid smoke; it has been described on p. 377. It is hardly applicable to the manufacture of sulphuric acid proper, but possibly to that of copper sulphate from waste sulphur dioxide. The same process, extended also to salts of manganese, iron, or tin, has been patented by Clark (for Daguin), No. 3669, 1888.

Sebillot (G. P. 109,484) passes SO_2 and air through towers packed with pumice, and receiving steam and more air, at temperatures below the boiling-point of sulphuric acid, without any nitric acid.

The "contact"-processes, founded upon the catalytic action of platinum or ferric oxide, are described in Chapter XI.

III. *Sulphuric Acid from Sulphates.*

The neutral sulphates of the alkalies, the alkaline earths, and lead are as good as unchangeable at a red-heat. The acid (primary) sulphates of the alkalies are first changed into pyrosulphates ($2NaHSO_4 = Na_2S_2O_7 + H_2O$); and the latter afterwards split up into neutral sulphates and sulphuric anhydride. This reaction, for obvious reasons, cannot be thought of for the manufacture of sulphuric acid proper, but only for that of fuming acid, under which head it has been noticed (comp. *suprà*, p. 968).

Most of the other sulphates are no better adapted for the manufacture of sulphuric acid. Only those whose metallic radicals are but very slightly positive, more particularly ferric oxide and alumina, and the *acid* sulphates of other radicals, yield up their sulphuric acid at a comparatively low temperature, and consequently all or the greater part of it undecomposed; the other sulphates split up at a much higher temperature, mostly decomposing into metallic oxides, sulphur dioxide, and oxygen, yielding only a small portion of their sulphuric acid as such or as anhydride. Even if it were otherwise, their high price would make their employment for the manufacture of sulphuric acid impossible; most of them are themselves produced by means of ready-made sulphuric acid. From even the cheapest and most easily decomposable of all the sulphates in question, ferric sulphate, only fuming oil of vitriol can be made, and that only under especially favourable circumstances, as shown p. 965.

There only remain the sulphates occurring in some abundance in nature as such, viz. those of baryta, lime, and magnesia. The first of these has hardly ever been seriously taken up for this purpose; but the sulphates of lime (gypsum) and of magnesia (kieserite) have very frequently been so.

Sulphuric Acid from Calcium Sulphate.

The enormous quantities of sulphuric acid occurring in nature in the shape of gypsum or anhydrite, and nearly worthless in this form, have occasioned many proposals for their technical utilization.

These, however, have never met with any success; and least of all can any prospect of it be held out nowadays, since an abundance of cupreous pyrites has been discovered, with which, so far as can be seen, no other material can compete in cheapness.

(1) *Production of sulphur dioxide from gypsum.*—Tilghman (English patent, Feb. 1st, 1847) passes steam over red-hot gypsum; CaO is said to remain behind, and SO_2, O, and a little SO_3 to escape. For the identical process, Polony obtained an Austrian patent in 1887 (Zeitschr. f. angew. Chem. 1888, p. 57).

Cary-Mantrand (Barreswil and Girard, Dictionn. de Chim. industr. i. p. 37) exposes ignited gypsum to a current of dry HCl (whence does he get this?). $CaCl_2$ is formed; and SO_2, O, and SO_3 escape.

O. Siemens (Dingl. Journ. clxix. p. 207; Wagner's Jahresb. 1863, p. 208) decomposes a fused mixture of gypsum and common salt by steam. There remains behind basic calcium sulphide with a little Na_2S, Na_2SO_3, and $Na_2S_2O_3$; the gases given off are SO_2, HCl, and H_2S; the latter is removed by conducting CO_2 and steam at the same time into the melted mass (?). This process is the subject of strongly adverse criticism by Buff (Wagner's Jahresb. 1864, p. 170), who shows that the decomposition observed has been produced merely by the red-hot iron which forms the material of the apparatus.

Kuenzi (Wagner's Jahresb. 1858, p. 95) fluxes gypsum with quartz, sand, clay, &c. to an easily fusible slag, whilst SO_2 and O escape. The same proposal was made by Frémy, and also by Archereau (ibid. 1865, p. 271), by the latter for the purpose of utilizing the oxygen as well.

O. Schott (Dingl. Journ. ccxxi. p. 442) ignites sodium sulphate, gypsum, and coal, in order to obtain a frit for glass-making; the SO_2 is to be conveyed into a lead chamber along with the other gas and converted into sulphuric acid.

Martin (Bull. Soc. Chim. xxi. p. 47) prescribes making an artificial sulphide by smelting 1700 parts of gypsum, 1000 of ferric oxide, and 500 of coal in a blast-furnace; this is to be burnt like natural sulphides. In this case *at most* a monosulphide of iron will be obtained, and that will cost more than the best pyrites.

Scheurer-Kestner asserts that calcium or magnesium sulphate, when calcined with ferric oxide, preferably together with fluorspar, gives off sulphuric anhydride.

Cummings (Amer. P. 342,785 ; E. P. by Lake, No. 7355, 1886) calcines a mixture of gypsum and clay in a suitable kiln; a hydraulic cement is formed, whilst SO_3, SO_2, and O are expelled, and are converted into sulphuric acid in the usual manner. [This is utterly hopeless with such dilute gases.]

(2) *Sulphuretted hydrogen from gypsum.*—Cary-Montrand (*l. c.*) decomposes a mixture of gypsum and coal at a red-heat by HCl gas, whereby $CaCl_2$, CO, H_2S, and S are formed.

Köhsel (Wagner's Jahresb. 1856, p. 57) decomposes gypsum, reduced by coal (that is, CaS), by carbonic acid, burns the H_2S given off to SO_2, and conveys the latter into lead chambers.

The same proposal has been made several times later, in connection with special proposals for utilizing the H_2S, of which only that of Chance (*suprà*, pp. 88 & 368) has been found to be practicable. At the present prices of pyrites even the Chance process does not seem to be economical in its application to gypsum.

Claus, Baranoff, and Hildt (G. P. 104,188) treat a mixture of calcium sulphate and coal in retorts. The gases formed by the reaction $CaSO_4 + C_2 = CaS + 2CO_2$ contain up to 90 per cent. CO_2 and less than 7·5 per cent. CO. They are made to act on CaS in the presence of water, so that $CaCO_3$ and H_2S are formed. The H_2S is passed into retorts containing anhydrous $CaSO_4$ at a red-heat. Here the reaction is

$$3CaSO_4 + 4H_2S = 3CaS + 4H_2O + 4SO_2.$$

This is always the initial reaction; but if an excess of H_2S is employed, this acts in the nascent state on SO_2 and free sulphur is formed by Dumas's reaction :

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

(3) *Sulphuric acid direct from gypsum.*— Von Seckendorff (Wagner's Jahresb. 1855, p. 54) decomposes gypsum by lead chloride at 75° into $CaCl_2$ and $PbSO_4$. A mixture of the latter salt (5 molecules) with hydrochloric acid of 33° Tw. (4 molecules) at 75° C. almost entirely decomposes into $PbCl_2$ (which is used for a new operation) and sulphuric acid (which is decanted and concentrated, the distilling HCl being condensed).

Shanks has patented Seckendorff's process for England (Oct. 9th, 1854).

Margueritte (patent of Dec. 22, 1854) decomposes lead phosphate by hydrochloric acid; hereby $PbCl_2$ and phosphoric acid are formed ; the latter, ignited with gypsum, yields calcium phosphate and sulphuric anhydride. The calcium phosphate and lead chloride, boiled together, regenerate lead phosphate, along with $CaCl_2$, which is worthless ; so that the hydrochloric acid is always lost.

Bandiner (Wagner's Jahresb. 1858, p. 102), Fleck (Fabr. von chem. Prod. aus thier. Abfällen, p. 131), Reinsch (Wagner's Jahresb. 1870, p. 167), and other authors mention the utilization of the sulphuric acid of gypsum by treatment with a solution of ammonium carbonate, whereby ammonium sulphate is formed. This process has been used in France for some time, but it acts only incompletely.

Van Denberg (U.S. P. 642,390) electrolyses calcium sulphate in a furnace in a molten condition in the presence of an excess of oxygen, thereby forming SO_3, and subsequently hydrating this.

IV. *Calcining Pyrites with Salt.*

Kenyon and Swindells (English patent, May 21st, 1872) calcine the chlorides of sodium or potossium with iron- or copper-pyrites, and treat the gas with nitric or chromic (!) acid in high towers, in order to convert the sulphurous into sulphuric acid; at the same time chlorine is given off. Wagner (Jahresb. 1874, p. 272) points out that in this process the sulphuric acid must remain behind in the shape of alkaline sulphates.

V. *By Electricity.*

Reynoso, in 1875, obtained a patent for causing electric sparks to pass through a compressed and cooled mixture of sulphurous acid and atmospheric air. The formation of SO_3 from a mixture of 2 vols. SO_2 and 1 vol. O by the electric spark was first observed in 1860 by H. Buff and A. W. Hofmann (Ann. Chem. Pharm. cxiii. p. 129) ; Deville (Bull. Soc. Chem. [2] iii. p. 366) has observed that in the presence of strong sulphuric acid, which absorbs the SO_3, the whole gaseous mixture can be united to form SO_3 in this way.

Wacker (Germ. pat. applic. W 10,532, 1894, and 10,591, 1895) proposes to prepare concentrated sulphuric acid by electrolysing water or dilute sulphuric acid through which a continuous stream of SO_2 is being passed. He employs an earthenware vessel, divided into two cells by a porous earthenware diaphragm. Into the anode cell a slow stream of SO_2 is introduced. In the cathode cell a magma of sulphur is formed, but little H_2S being given off

If hydrochloric acid is added, no sulphur is separated, the chlorine formed by electrolysis directly oxidizing the SO_2. Other oxygen carriers may also be employed, such as sodium chloride or sodium sulphate, which acts by forming persulphuric acid; or else chlorates, nitrates, and so forth. [This process, in its present form, is a very peculiar one.] Compare also Van Denberg's patent, p. 1100.

A. C. Johnson (U.S. P. 659,236) sends a series of electric sparks into a chamber containing vaporous sulphuric-acid gas [?] and introduces oxyhydrogen gas, which is exploded by the electric spark, whereby the acid-laden particles of moisture may be precipitated [?].

C. B. Jacobs (U.S. P. 704,831, July 15, 1902) forces SO_2 through a porous anode, and oxidizes it by the oxygen of water decomposed at the anode. The SO_2 is oxidized in the lower region of the bath, and the oxidation product is retained remote from the cathode. A sufficient current-density is maintained at the cathode to prevent the access of SO_2 to it and to cause the rapid escape of hydrogen. The inventor claims (Min. Ind. vol. x. p. 602) to attain an electrolytical efficiency of 54 per cent. with a potential difference of 2 volts and a current density of 15 to 20 amperes per square foot of anode surface.

A new process for the electrolytic preparation of sulphuric acid is described in A. Friedländer's German patent No. 127,985. Dilute sulphuric acid or water is electrolysed with application of diaphragms in such a manner that at the same time sulphur dioxide is passed into the anode cells, separated from the cathode cells in such a manner that the gaseous contents cannot communicate, keeping the contents under the requisite pressure, and conducting away the heat of reaction by internal or external cooling. In the cathode cells the reaction is $H_2SO_4 = H_2 + SO_4$. The hydrogen is conducted away; the SO_4 ions migrate through the diaphragm to the anode, where they find SO_2 and react with it thus: $SO_4 + SO_2 = 2SO_3$. The liquids remain perfectly clear, and there is no separation of sulphur, as in previous attempts at the electrolytic preparation of sulphuric acid from SO_2.

Boehringer and Söhne (G. P. 117,129) attain the same object by adding to the sulphuric acid in the anode cell manganous sulphate, which serves as an oxygen carrier and thus converts SO_2 into sulphuric acid, ultimately up to sp. gr. 1·78.

CHAPTER XIII.

BY-PRODUCTS OF THE MANUFACTURE OF SULPHURIC ACID.

The most important of these in the case of cupreous pyrites is the copper itself, along with the iron oxide (obtained in this case in a sufficiently pure form), sometimes also with silver; we shall treat this subject more in detail later on. From non-cupreous pyrites, however, iron and zinc are only exceptionally obtained. We do not, of course, refer to metals whose production is the principal object of the whole process.

Besides, thallium and selenium may be mentioned as by-products of sulphuric-acid making.

The cinders from non-cupreous pyrites (as to their composition comp. p. 316) are frequently used *as ballast for making roads*; they yield very firm, dry, and even roads, which, however, are soon ground into dust by vehicular traffic, and in wet weather are then very muddy. Besides, the rain-water washes out iron and zinc sulphates, and may carry these into neighbouring wells (Sarrazin, 'Archiv der Pharmacie,' ccix. p. 418).

These cinders have frequently been proposed for the *absorption of sulphuretted hydrogen gas,* and really seem to have been here and there employed for purifying coal-gas and for disinfecting cesspools (Zeitsch. für chem. Grossgew. i. p. 70). This, however, cannot be done extensively, as the cinders do not act anything like so energetically upon H_2S as precipitated ferric hydroxide or bog-iron ore, and therefore the purifying-apparatus would have to be made of enormous dimensions. Probably more success is obtained in the manufacture of ferrous sulphate by neutralizing the sulphuric acid formed in the oxidation of bituminous lignite slates; formerly metallic iron used to be employed for this purpose.

It has also been proposed to utilize the pyrites-cinders or the "purple ore" (see below) for decomposing solutions of alkaline sulphides, but in this case the action is too imperfect. But after converting the ferric oxide into a "ferrite" by ignition with soda, the compound thus formed has an energetic action upon solutions of alkaline sulphides, upon which are founded the processes of Arrott and of Ellershausen (comp. Vol. II.).

A. & P. Buisine (see Vol. II.) employ moistened pyrites-cinders *for absorbing hydrogen chloride* from gases containing very little HCl. Or else they convert them into *ferric sulphate* (Compt. Rend. 1892, cxv. p. 51) by heating with sulphuric acid 60° B. not above 300° C. The resulting grey mass is hardly soluble in water, but becomes soluble by hydration at somewhat higher temperatures. The product can be employed direct as a very cheap ferric salt, or converted into *ferrous sulphate* by digestion with iron. [This is indeed very easy, as the author has convinced himself; ferrous sulphate is manufactured in this manner both more cheaply and more conveniently than by dissolving scrap-iron in sulphuric acid. The mass obtained by heating the cinders with Glover-tower acid is dissolved in hot water, the solution is digested with scrap-iron until the reduction to $FeSO_4$ is complete, evaporated to 27° or 28° B. (measured at 90° C.), and allowed to crystallize, a number of strips of iron being suspended in the vat.]

Ferric chloride can be made by absorbing the gases from salt-cake furnaces in cylinders charged with pyrites-cinders, which takes place with evolution of heat.

Buisine (Germ. pat. 73,222) also describes a process for recovering from pyrites-cinders *ferrous sulphate and free sulphur* by the following reactions :—

$$\begin{aligned} Fe_2O_3 + 3H_2SO_4 &= Fe_2(SO_4)_3 + 3H_2O, \\ Fe_2S_3 + 2H_2SO_4 &= 2FeSO_4 + S + 2H_2S, \\ FeS + H_2SO_4 &= FeSO_4 + H_2S, \\ H_2S + Fe_2(SO_4)_3 &= 2FeSO_4 + H_2SO_4 + S, \\ 3H_2S + H_2SO_4 &= 4S + 4H_2O. \end{aligned}$$

The ultimate products of these reactions, apart from steam, are only ferrous sulphate and free sulphur, which are easily separated.

Arnois (Amer. pat. 413,428) seeks to convert burnt pyrites into a useful *paint* by treating it at a dark red-heat in an ordinary atmosphere with a mixture of calcium carbonate and common salt in various proportions. [No doubt the treatment applied to the residue from the manufacture of Nordhausen acid (*suprà* p. 963) could be applied to pyrites-cinders as well; but only in the case of very pure ores, like the Aguas Teñidas, can products be obtained of sufficient purity for the above-named purpose.]

Mills (G. P. 86,589) proposes to reduce pyrites-cinders to iron *protoxide* for use as a black paint or in pharmacy. The cinders are sifted, ground, mixed with "amorphous" metallic iron (probably "spongy iron" is meant, comp. below), and heated to a red-heat in the absence of air. The quantity of metallic iron required depends upon the percentage of Fe_2O_3 and Fe_3O_4 present in the cinders; the latter requires much higher temperatures for reduction. For pharmaceutical purposes the impure protoxide thus obtained is dissolved in dilute sulphuric acid, precipitated by caustic soda solution and the dried precipitate reduced by iron. [There are several doubtful points in this proposal.]

Manufacture of Iron from Pyrites-cinders.

The most important use of pyrites-cinders is for the manufacture of iron, either in blast-furnaces or in the manufacture of wrought iron from pig-iron in puddling-furnaces, Siemens-Martin furnaces, &c.

Formerly ordinary pyrites-cinders (from non-cupreous ores) could not be employed by making iron, because they contained at least 4 per cent., and usually more than this, of sulphur. One of the first attempts at utilizing such cinders for the manufacture of iron was made at the Chauny works, which, in 1873, exhibited iron made from non-cupreous pyrites-cinders, desulphurized by repeated roasting in a Perret's kiln in thin layers. For this purpose the plates of this kiln were charged alternately with cinders and with fresh pyrites, the heat produced in the burning of the latter causing a supplementary roasting of the cinders (Hofmann's 'Bericht,' 1875, i. p. 164).

Since that time very much progress has been made in treating the pyrites, both lumps and smalls, in such manner as to desulphurize it more completely; but this can only be done if the ore is pure, *i. e.* contains very little or no zinc and lead sulphides. Such pure ores can be burned in lumps down to 2·5 or even 2 per cent., and in the shape of dust even below 1 per cent. sulphur in the cinders, and in this case they can be smelted like ordinary (somewhat impure) iron-ores. In England, during 1902, the maximum percentage of sulphur allowed by the iron-works buying pyrites-cinders was 2 per cent., in Germany 1·5 per cent.

It has frequently been attempted to employ the cinders of small ore in larger quantities for smelting in a blast-furnace without stopping it up, by conglomerating them in different ways, but without much success. A patent was taken out by J. Cahen for this purpose (10th June, 1875). He moulds the cinders into suitable cakes with tar, peat, and limestone, and smelts these in a blast-furnace; the pig-iron is said to be very pure, the sulphur being absorbed by the lime, and the peat assisting in the formation of volatile phosphuretted hydrogen (?). J. L. Bell also moulds the small ore with lime into bricks, which harden by drying, and uses them in a blast-furnace. All such artificial conglomerates are soon crushed by the great pressure in the blast-furnace, and thus act like the loose powder.

Henzel (Germ. pat. appl. H No. 12,573) mixes pyrites-cinders with from 5 to 40 per cent. ground clay and a little water, and charges the mixture (which may be previously moulded into bricks) by means of spades into a blast-furnace. The powdered ore is kept together by a superficial fusion of the aluminium silicate, but remains porous and permeable for the reducing gases. [One cannot understand how such a simple application of extremely old technical principles could form the subject of a patent.]

The Georgs-Marien-Hüttenverein (Germ. pat. 61,061) heats bricks, moulded from pyrites-cinders, by a special fire to the sintering point.

Wüst (Germ. pat. 82,120) mixes pyrites-cinders with 7 per cent. silicate of soda, moulds the mixture by pressing, and exposes it at a moderate temperature to the action of carbonic acid, by which free silica and sodium carbonate are formed. The silica acts as a cement; the sodium carbonate promotes the fusion of the slag, and prevents the sulphur contained in the cinders from passing into the pig-iron. [If the application of silicate of soda is not too expensive, its decomposition would be more easily and quickly obtained by the waste acid liquors formed at most works.]

The Duisburg Copper-works (Germ. pat. appl. D No. 6242) mix pyrites-cinders with ground furnace scale (magnetic oxide of iron) or similar slags, if necessary also with lime, mould the mixture into bricks and dry these. According to whether lime has been employed or not, from 5 to 20 per cent. of slags is required. The product is sufficiently firm for use in blast-furnaces; owing to the admixture of slag, it is also porous and accessible for the reducing gases.

In England, bricks of purple-ore are made without any cementing substance, merely by strong pressure, for use in Siemens-Martin furnaces (Zsch. f. angew. Chem. 1894, p. 9).

Richters (Dingl. Journ. cxcix. p. 292) investigated the application of pyrites-cinders in a coke blast-furnace by the analysis of all the products. With a charge of 38 calcined magnetic iron-ore, 1½ black band, 25·5 cinders (containing 4·35 per cent. SO and 1·53 S in other forms), and 35 limestone, under especially favourable circumstances, pig-iron with only 0·022 per cent. of sulphur was obtained; when, however, the temperature was lower, even with only 12 pyrites-cinders to 53·5 other iron-ore and 33·5 limestone, the pig-iron showed 0·049, 0·088, 0·096, 0·224 per cent. of sulphur. With a mixture of 19·2 pyrites-cinders, 46·5 other iron-ores, 30·1 limestone, and 4·2 potsherds the sulphur in the pig-iron varied from 0·033 to 0·060 per cent.; by adding another 3·77 potsherds the sulphur was increased to 0·110–0·146 per cent. The pig-iron poorer in sulphur always contained a great deal of silicon, up to 3·485 per cent.

The cinders from roasting Schwelm pyrites are said to furnish an excellent material for Bessemer pig, as they contain very little phosphorus and copper, which are so injurious to the quality of steel. F. Schmidt (Berg- u. hüttenmänn. Zeit. 1878, p. 68) states the composition of these cinders as follows :—

Ferric oxide	90·547	=65·0056 Fe.
Ferrous oxide	0·520	
Iron bisulphide	0·574	
Lead sulphide	0·142	
Copper sulphide	0·026	
Manganous oxide	0·463	
Alumina	1·448	
Lime	0·388	
Magnesia	0·220	
Carried forward	94·328	

Brought forward	94·328
Sulphur trioxide	1·110
Phosphorus pentoxide	0·035
Silica	3·447
Moisture	0·897
	99·817

Paur (Germ. patent No. 8730, May 22, 1879) proposes to treat the crushed pyrites-cinders with a solution of alkaline permanganate, by which sodium sulphate and MnO_2 are formed. The first is washed out; and the residue forms a manganiferous iron-ore, free from sulphur (but in all probability far too expensive).

Recovery of Zinc from Pyrites-cinders.

Pyrites containing zinc, such as the Westphalian ore from Meggen, cannot possibly be desulphurized in the burners so well as purer ore, owing to the great heat required for decomposing the zinc sulphate. The cinders from such ores contain both too much sulphur and too much zinc to be useful for the manufacture of iron without a special treatment for removing these impurities.

P. W. Hofmann ('Zeitschr. d. Vereins deutscher Ingenieure,' xviii. p. 521) proposed the following process for utilizing the cinders from Westphalian pyrites, which sometimes contain 6 per cent. of zinc:—The cinders contain the zinc as sulphate, which is only decomposed at a much higher temperature than is attainable in a pyrites-burner. The zinc sulphate can be washed out by water at 40°; but it contains too much iron sulphate to be saleable. If, however, a solution of 1·25 sp. gr. be mixed with a proportion of NaCl equivalent to the sulphuric acid contained in it, and heated to 30° C., a lye of 1·38 sp. gr. is obtained, from which, on cooling, such a quantity of Glauber's salt crystallizes that this alone pays all expenses. The mother-liquor contains chloride of zinc with more or less common salt and the sulphates of iron, zinc, and sodium. If evaporated to 1·60 sp. gr., all foreign salts are separated, and a solution of zinc chloride, with mere traces of sulphates and of iron, remains behind, which can be employed directly for pickling railway-sleepers. The residue from lixiviating the sulphates is allowed to lie a few days in the air to dry; most of it then falls to powder. When this is passed through a sieve, the fine dust is found to be almost free from sulphur, the rougher particles containing nearly all the sulphur in the shape of FeS. The dust might be employed in a blast-furnace.

At the Aussig works formerly the crude zinc sulphate obtained in just the same way was worked up by the addition of calcium chloride (waste lye from the recovery of sulphur) into "pearl-hardening" and zinc chloride. Owing to the want of a sufficien market, this manufacture has been discontinued.

Creutz (Chem. Ind. 1883, p. 258) remarks that Hofmann's process has not been much used, because the reactions are not s smooth as represented. The sodium sulphate remaining in th zinc-chloride liquor is prejudicial to its employment for pickling timber. Nor were better results obtained by mixing the solutions of sodium chloride and zinc sulphate in the cold, as recommended by the American patent No. 236,051. The formation of doub salts of zinc and sodium is the cause of this difficulty. It i therefore best to employ calcium chloride (comp. above) in th following manner:—The pyrites-cinders are exposed to the weathe as long as possible to oxidize the iron and manganese compounds and the sulphurous acid. They are then lixiviated with cinde containing 3 per cent. zinc; a solution of zinc sulphate is obtaine of spec. grav. 1·16, containing next to no iron and only traces manganese and cobalt. This liquor is mixed with waste calcium-chloride liquor from the Weldon process, of spec. grav. 1·11 leaving a small excess of zinc sulphate. Calcium sulphate is pre-cipitated and is filtered off. The clear liquor, of spec. grav. 1·075 is boiled down in an iron pan with top heat, and a little bleaching-powder is added to precipitate manganese and cobalt as peroxide At a concentration of 1·5, the last traces of calcium sulphate a precipitated, and the clear liquor now contains only zinc chlorid with a little zinc sulphate, no more than is contained in the liq obtained by dissolving scrap-zinc in commercial hydrochloric ac This process has the drawback of requiring fuel for boiling do the liquor, but it furnishes a liquor entirely fit for pickling woo The expense of boiling down is saved when the crude solution zinc chloride is treated for the preparation of zinc hydrate purifying soda-liquors from sulphides) by addition of lime, a filtering through a sand filter.

Egestorff's Salzwerke (G. P. 23,712) purify pyrites-cinders fr zinc by weathering, lixiviating, adding to the liquor calcium or barium carbonate, and treating it with a current of air. In this case the iron is quickly precipitated, and there is obtained on the one hand an iron-ore free from zinc, on the other hand zinc salt free from iron.

The Königshütte Berg- und Hüttenverwaltung (G. P. 28,465) roast pyrites-cinders, containing zinc, with common salt, and lixiviate with weak hydrochloric acid. The liquor in case of need is freed from copper and is cooled down to such a temperature that sodium sulphate crystallizes out. The zinc remains in the mother-liquor, and is recovered in the usual manner, probably chiefly in the shape of crystallized zinc sulphate.

Kosmann (Fischer's Jahresb. 1886, p. 268) regards all the processes hitherto employed for the above purposes as of doubtful economic value.

Herberts (G. P. 38,780) treats pyrites-cinders containing zinc in an iron boiler under pressure with steam; the sulphates of zinc and iron are dissolved, ferric oxide remains behind. Another patent of the same inventor (G. P. 41,333) contains some improvements.

Riemann (G. P. 38,072; Fischer's Jahresb. 1887, p. 510) contends that only a third part of the zinc is dissolved in this manner. He therefore returns to the roasting with salt, but adds ferric sulphate, obtained by treating ground pyrites-cinders with hot sulphuric acid. A mixture is made of the cinders with 8 or 10 per cent. of crude ferric sulphate, and 15 or 18 per cent. of common salt, and is roasted for several hours in a reverberatory or muffle furnace, with access of air, at a temperature not exceeding 500° C. The product can be lixiviated with water alone, without adding any acid; the washed residue contains only 1 or 1·5 per cent. zinc, 0·3 or 0·6 sulphur, and 55 iron, and is therefore a useful iron-ore. The liquor contains any copper present in the ore, zinc chloride, and sodium sulphate. These salts cannot be separated, as asserted, by boiling down to spec. grav. 1·53, owing to the formation of double salts of zinc and sodium, but by concentrating the liquor, when at spec. grav. 1·32 to 1·36, in the cold by means of a vacuum. It is claimed that this process really permits of utilizing the cinders from German pyrites, hitherto so troublesome.

Electricity has also been invoked for precipitating the zinc from the liquors obtained by the above-mentioned processes, but this does not seem to be economical.

Perino (G. P. 46,748) makes an intimate mixture of the ore with ferric nitrate, and exposes this to gentle heat; about 50° nitrous fumes are evolved and zinc sulphate is formed, whilst the iron sulphide is less easily acted upon. The process is finished at about 150° or 200°. [This cannot pay, even when recovering as much as possible of the nitric acid from the fumes.]

From the zinc solution, obtained by roasting the cinders with salt and lixiviating, a valuable paint can be obtained by precipitating, with a solution of barium chloride, a mixture of barium sulphate and zinc sulphide. This mixture is called *lithopone* and is largely employed as a non-poisonous substitute for white-lead. It was exhibited at Düsseldorf in 1902, by the Schalke Chemical Company, which prepares it from the cinders of Westphalian pyrites.

Kellner (E. P. 7028, 1901) grinds pyrites-cinders, treats them with aqueous sulphurous acid in order to convert the zinc into bisulphate, oxidizes this by air to sulphate, converts this into chloride by means of NaCl or KCl, and electrolyses the $ZnCl_2$.

Recovery of Thallium and Selenium.

In the flue-dust and the chamber-deposit of many descriptions of pyrites the rare metals ***selenium*** and ***thallium*** have been found. The former has hitherto no industrial application, apart from the employment of crystalline selenium in photometry, as its electrical conductivity changes in proportion to the intensity of the light that falls upon it.

Thallium, however, is manufactured on a comparatively large scale at Aussig and Mannheim; and it might possibly be found useful for optical glass, replacing the alkali: owing to its very high atomic weight (204) it gives, along with red-lead and quartz the specifically heaviest and consequently the most refractive glass hitherto known (Lamy).

The preparation of thallium from the flue-dust of Westphalian pyrites has been described by Schaffner (Wagner's Jahresb. 1871, p. 1). The flue-dust was collected in a large brick chamber without being exposed to the action of nitrous vapours, the chambers being fed directly with nitric acid. It is coloured by ferric oxide, contains much arsenious acid, ferric sulphate, some zinc oxide, lead oxide, traces of antimony and silver, thallium sulphate, &c. Carstanjen (Wagn. Jahresb. 1868, p. 10) found in it 3·5 per cent. thallium. On the sides of the chamber crystals were found of the compound As_2O_3 and SO_3, discovered by Reich. The flue-dust is lixiviated by boiling with steam, with the addition of a little sulphuric acid, as a portion of the thallium seems to be present as basic sulphate, which would escape solution. After settling, the clear portion is siphoned off and filtered through calico; the residue is boiled again. From the liquid the thallium is precipitated as protochloride. The very impure reddish precipitate is washed with cold water and converted into sulphate by hot concentrated sulphuric acid, the heating being continued till all excess of acid is driven off. The sulphate is dissolved in water, filtered, and again precipitated by hydrochloric acid, the TlCl now being separated almost in the pure state. If it is not yet pure, especially if it contains arsenic, the operation must be again repeated. In order to remove all arsenic, sulphuretted hydrogen is conducted into the solution of thallium sulphate, which precipitates all the arsenic with small quantities of thallium; the latter is precipitated from the filtrate by hydrochloric acid as perfectly pure TlCl, and converted into sulphate as above. The latter is reduced to metallic thallium by digesting its solution in a porcelain or stoneware dish with metallic zinc. The spongy metal obtained is washed with distilled water, pressed between blotting-paper, and melted in an iron or porcelain crucible, hydrogen or coal-gas being conducted through to prevent any oxidation; the heat should not be too strong, because it might volatilize the thallium. The melted metal, similar to mercury, is cast into small rods in paper moulds. It should be kept in boiled water free from air, the vessel being closed whilst the water is boiling; but even then the latter after a short time shows an alkaline reaction. It is best kept in a solution of zinc sulphate. It can also be obtained well crystallized by Woehler's process, viz. by suspending in the thallium solution a beaker with its bottom cut off, and its lower part closed with a bladder tied round: this is filled with water up to the level of the solution outside; a zinc plate is suspended in the water, and the latter connected with a platinum wire, which dips into the thallium solution and is bent into a spiral below the bladder.

Krause (Dingl. Journ. ccxvii. p. 323) observes that the treatment of thallium protochloride with concentrated sulphuric acid is very unpleasant work in large quantities. He has found that the decomposition can be quickly and completely effected by a weak solution of Glauber's salt, say 4° to 7° Tw. He lixiviates the fine dust in a cask with water and steam, siphons off the settled liquid into a second cask, and adds to this solution of thallium sulphate hydrochloric acid; the TlCl subsides very quickly, if the liquid is well agitated, for instance by a current of air. After a short rest the clear liquid is run off, the cask is filled up with pure water, heated by steam, and crystallized sodium sulphate added till the solution shows 7° Tw. After strong agitation the decomposition is complete, and the liquid is siphoned off into a third cask, which is placed somewhat lower; here it is acidulated with sulphuric acid and the thallium precipitated by zinc. Similarly to Schaffner, he washes the sponge with water free from air, presses and melts it. This process permits working continuously and without contact with fire.

Nietzki has made very detailed communications on thallium (Wagner's Jahresb. 1876, p. 4). He found in the flue-dust of the Duisburg chemical works, where Westphalian pyrites is used, 0·1 to 0·2, sometimes even 1 per cent. thallium. The precipitation as TlCl is incomplete: it is true that TlCl, which is soluble in 500 parts of water, is much less so in the large excess of hydrochloric acid actually employed; but there remains even then 10 per cent. of the thallium present in the mother-liquor. Much more complete is the precipitation of thallium by potassium iodide as TlI, even from very dilute solutions of flue-dust. Therefore both the mother-liquors from the TlCl precipitate and the dilute extractions of flue-dust are afterwards treated with KI. By boiling the TlI with sodium sulphide the iodine is recovered as NaI; and the insoluble Tl_2S is worked up for Tl_2SO_4 along with the TlCl. From the sulphate the thallium is obtained by electrolysis, to avoid its contamination with zinc. In this case crude thallium sulphate can be employed; whilst direct reduction with zinc is troublesome, owing to the evolution of arseniuretted hydrogen and the reduction of ferric salts, the ferrous sulphate soon forming a crust over the zinc and making it inactive. Nietzki even employs KI for volumetrically estimating thallium; but the solutions must not be too dilute.

Stolba's process (Wagner's Jahresb. 1874, p. 1), allowing a thallium-alum or thallium-iron-alum to crystallize from concentrated solutions of flue-dust, is only adapted for a substance extraordinarily rich in thallium.

Woehler (Ann. Chem. Pharm. clxiv. p. 74) states that thallium is more simply produced by fluxing the chloride with sodium carbonate and carbon. 20 parts TlCl, 8 parts of dry $NaCO_3$, and 1 part of lampblack are mixed together and fluxed in a fire-clay crucible at a moderate red-heat. A small loss occurs by some chloride volatilizing; this can be avoided by stirring up the mixture with water, drying, and then fluxing.

Selenium was discovered (in 1817) by Berzelius in the chamber-deposit of the sulphuric-acid works at Gripsholm, at which Fahlun sulphur (obtained in roasting ores) was used. It also occurs in volcanic sulphur, *e. g.* 0·264 per cent. in the solfataras of Naples, according to Phipson (Chem. News, v. p. 337)—principally, however, in many descriptions of pyrites; so that the chamber-deposit of the Mansfeld and Oker works is the best source of it. Selenium occurs in several allotropic modifications, in regard to which we must refer our readers to the chemical treatises. Its spec. grav. is given as 4·26 to 4·8, melting-point 400°, boiling-point about 700°. Selenium always occurs in very small quantities; but its characteristic reactions cause it to be easily discovered, and it becomes very much concentrated in the deposit of flue-dust. Some Harz works' deposit is said to contain 10 per cent., that of the Eisleben works 9 per cent. of selenium; annually several cwt. are obtained in this way (Böttger and Kemper, Wagner's Jahresb. 1860, p. 169). On selenium in French sulphuric acids communications have been made by Kuhlmann, Personne, and Scheurer-Kestner (ib. 1872, p. 246); comp. also Lunge (Chem. Ind. 1883, p. 128) and Davis (J. Soc. Chem. Ind. 1883, p. 158).

The deposit contains free selenium, as the selenious acid formed by burning is reduced by sulphurous acid. Otto (Lehrbuch d. Chem. 4th ed. i. p. 633) digests the deposit, previously washed with water, with aqua regia to oxidize the selenium, adds sulphuric acid, evaporates to dryness, driving off the other acids, treats the residue with water, and from the solution, by cautious addition of ammonium sulphite, first precipitates white mercurial chloroseleniate, then from the filtrate, by more ammonium sulphite and sulphuric acid, the selenium itself. From the mercurial percipitate the selenium can be obtained by oxidizing with nitric acid, evaporating, neutralizing with sodium carbonate, fluxing with potassium nitrate, boiling with hydrochloric acid in order to reduce SeO_3 to SeO_2, and precipitating the selenium from the solution by SO_2.

Liebe (Wagner's Jahresb. 1860, p. 178) extracts the oxidized mass, after evaporation with sulphuric acid, with water, neutralizes with soda-ash, evaporates to dryness, mixes the residue with an equal weight of sal-ammoniac, calcines the mass in a porcelain dish (when the sal-ammoniac reduces the SeO_2), and washes with water, pure selenium remaining behind.

Böttger (Dingl. Journ. clxxvi. p. 405) extracts the selenium from the chamber-deposit washed with water by means of a concentrated solution of neutral sodium sulphite, and filters it into dilute hydrochloric acid, which at once precipitates the selenium.

Nilson (Ber. d. deutsch. chem. Ges. vii. p. 1719) describes the working-up of the Fahlun chamber-deposit for selenium. This cannot well be done by Otto's process; it is better to employ potassium cyanide, 2 parts of which yield 1 part of selenium. The washed deposit needs only to be digested with a concentrated solution of potassium cyanide at 80° to 100° C. till its red colour has just been turned into pure grey; the residue is washed with boiling water, filtered, and hydrochloric acid added to the solution; selenium at once precipitates in cherry-red flakes, as the liberated selenocyanic acid is almost instantaneously decomposed into selenium and hydrocyanic acid; the sulphur dissolved at the same time remains in solution as sulphocyanic acid. The selenium thus obtained contains only a little copper, iron, and perhaps traces of mercury; it is obtained quite pure by dissolving in nitric acid, evaporating to dryness in a water-bath, subliming the anhydride in a current of dry air, and treating its solution with sulphurous and hydrochloric acids.

Kienlen (Bull. Soc. Chem. [2] xxiv. p. 440) showed that the selenium, being reduced by SO_2 in the Glover tower, is dissolved in the sulphuric acid, to which it sometimes imparts a blood-red colour. When diluting it with three times its bulk of water, the selenium is precipitated. Glover acid contains up to 17·3 millig., chamber-acid 22·3 millig. per kilog. If such sulphuric acid is employed for the manufacture of hydrochloric acid, the selenium is volatilized together with HCl and is deposited in the first receivers as a reddish mud containing 41 to 45 per cent. Se, whilst the hydrochloric acid holds up to 21·4 millig. Se per kilog. The selenium is extracted from the mud by chlorine, which forms selenious and selenic acid. When the red colour has been destroyed, the mass is filtered, the filtrate is boiled with hydrochloric acid, and the selenium precipitated by sodium sulphite.

Bornträger (Dingl. Journ. ccxlvii. p. 505) found in the red mud from Glover-tower acid (made from Rio-Tinto pyrites), after washing and drying, 12·60 per cent. Se (with 76·30 $PbSO_4$ &c.). He obtains the selenium from it by heating it in fireclay retorts at a red-heat, with exclusion of air, as a black metallic sublimate, which is freed from As_2O_3 and SeO_2 by washing with strong caustic soda.

Divers and Shimosé (Chem. News, No. 1256) found in sulphuric acid made from Japanese brimstone 0·37 grm. tellurium and 0·15 grm. selenium per litre, and in the sediment from the same acid 10·5 per cent. selenium and 1·2 per cent. tellurium. Shimosé (ibid. No. 1260) further describes the process employed by him for separating selenium and tellurium, viz., neutralizing the sediment with sodium carbonate, removing the selenium by digesting with concentrated solution of potassium cyanide at a gentle heat (at first cold), diluting the mixture with water, and heating nearly to boiling. The solution, containing the selenium, is treated with hydrochloric acid in order to separate the Se; on the other hand, the sediment from which the cyanide solution has been decanted yields tellurium by a treatment with sulphuric acid and a little nitric acid, and passing H_2S through the solution obtained.

The Mansfeld Kupferschiefer Mining Company (Wagner's Jahresb. 1876, p. 297) in 1875 produced

Selenium	2·38 kil.,	value £18.
Flue-dust containing selenium	4½ ,,	,, £6 2*s*.

The Extraction of Copper from Pyrites-cinders.

This manufacture cannot properly be regarded as a by-work done in sulphuric-acid making; with as much, if not with greater, right the latter might be considered a secondary branch of the extraction of copper, since in the cupreous ores the value of the copper mostly exceeds that of the sulphur contained in them; but if the value of the final products be counted, that of the sulphuric acid certainly mostly far outweighs that of the copper. Even in the large English works nowadays the extraction of copper from the cinders is rarely done in the chemical factory itself; the former is concentrated in a few works erected in the centres of the chemical trade, which receive the burnt ore from a whole group of chemical works. One of the largest pyrites-mining companies, the Tharsis Sulphur- and Copper-extracting Company, supplies its ores to the consumers only on condition of returning the burnt ore to the copper-works belonging to the same Company. A similar establishment was founded at Duisburg by a number of Rhenish manufacturers, likewise based on the extraction of Spanish pyrites-cinders. Although the production of copper thus does not belong to the usual cycle of vitriol- and alkali-works, yet it is most intimately connected with it, especially in Great Britain; and a short description of that production does not seem out of place here.

The percentage of copper in the ores in question (comp. p. 54) is mostly so small, rarely above 4 per cent., that its extraction by smelting would not pay. This can only be made possible at the outset by carrying on the first necessary operation (the calcining or burning) in such a way that the calcining-gas does not go away into the air, but is taken into lead chambers and sulphuric acid made of it, which helps to pay for the ore. But something else is necessary in practice. The cinders from burning the ore are still too poor in copper to be smelted in the usual way. They might possibly be smelted to coarse metal, with a mixture of a little green pyrites, siliceous sand, and slags; and this coarse metal might be sent to copper-works for further treatment; but in that case only a portion of the copper would be obtained, and the expense would be barely covered. When the quantity of poor ore coming into the market became larger, this way of utilizing it was out of the question. Other drawbacks in smelting for coarse metal, as they were observed at Oker, will be mentioned below.

Accordingly, since 1865, the copper of poor ores is always extracted *in the wet way.* From time immemorial the pit-waters arising from weathered ore have been precipitated by metallic iron, and *cement-copper* obtained in this way; but the processes for converting the copper purposely into such compounds that it becomes capable of being dissolved and precipitated, all date from a recent period. Exact descriptions of the former processes are found in Percy's 'Metallurgy,' more recent processes in Stölzel's 'Metallurgie,' i. p. 714, and in Hofmann's 'Bericht' of 1873, p. 885 (this article is from the pen of Professor Kerl). Most of the volumes of Wagner's 'Jahresberichte' contain the literature of this branch.

It is beyond the scope of this book to enter specially upon all the proposed or really carried-out processes for copper-extraction in the wet way; we must refer the reader to the authorities just mentioned, and we shall only describe that process which for a number of years has been exclusively employed for working up the cinders from vitriol-works, viz. the *roasting with salt,* followed by the *precipitation by means of iron.* It appears that the interesting process of lixiviating by means of ferrous chloride, originally proposed by Schaffner, but best known in the shape given to it by Sterry Hunt and Douglas, is not in use at vitriol-works or at the copper-works in immediate connection with these; we must therefore, in respect of this also, refer to the originals.

The first attempts in this way seem to be referable to Hunt (patent of Jan. 21, 1840), and especially to Longmaid (patents of Oct. 20, 1842, and Jan. 1, 1844). The latter exactly described the principles of the process, as it is carried out to the present day, certainly with a view to making salt-cake and chlorine as the chief products; and he also worked it out on a large scale; so that he must be regarded as the founder of the wet extraction of copper. Certain small improvements were patented at different times—for instance, by Gossage on July 17th, 1850. We find much latter, in 1856, the process started with a good deal of noise as a novel one, by Bechi, of Florence, and Haupt, of Freiberg, for working the ores at Capanne Vecchie (Wagner's Jahresb, 1858, p. 68). It is strange that, 16 years after Longmaid, such a distinguished metallurgist as Gruner should ascribe the success of Bechi's process less to the influence of the common salt than to the fine grinding. Bechi and Haupt's process was patented in England in the name of Hähner on March 7th, 1856; it differs from Longmaid's process merely by much greater complication, such as calcining three times instead of once, and has long since been given up. Schaffner (Wagner's Jahresb. 1862, p. 119; 1871, p. 139) improved the process in several respects; but it was carried out on a large scale chiefly in England, by Phillips, Henderson, Tennant, and others.

Spongy iron was first employed by Gossage; it was again patented by Aas in 1861, and by G. Bischof in 1862.

The process now generally employed in England has been principally described by Clapham (Chem. News, xxiii. p. 26), Wedding and Ulrich (Wagner's Jahresb. 1872, p. 152), Gibb (Chem. News, xxxi. p. 165, and several publications of the Tyne Chemical Society), by myself (Dingl. Journ. cciv. p. 288, ccxiv. p. 466, ccxv. pp. 54 & 229, ccxix. p. 323); the process at Oker by Bräuning (Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen, 1877, p. 156). Several more recent descriptions, *e. g.* that by Egleston (Fischer's Jahresb. 1886, p. 170), contain nothing of any importance. A paper by Bode (Dingl. Journ. ccxxxi. pp. 254, 357, and 428) gives a very complete survey of all the previous ones. The notes of E. A. Mebus, published by Jurisch, are also of interest, especially concerning the recovery of silver (Chem. Ind. 1894, p. 378). The process and plant used at Natrona, near Pittsburg, are described by Clemmer, 'Mineral Industry,' vii. p. 197, and ix. p. 283. In the following description the above sources are used, along with notes taken by me at several copper-works.

The three most important ores employed in the English factories contain from 47 to 49 per cent. of sulphur, and the following quantities of copper and silver:—

	Copper. per cent.	Silver. ounces, troy, per ton.
Rio-Tinto	3·80	1·20
Tharsis	3·50	0·75
San-Domingo	3·70	0·75

(N.B.—An ounce troy is =480 grains; there are 32,666 ounces troy to the ton.)

The "ordinary copper-ores" at Oker generally consist of 60 per cent. iron-pyrites, 23 per cent. copper-pyrites, 6 blende, 2 galena, 9 gangue (complete analyses, p. 84).

The percentage of sulphur in the cinders as they are supplied by the acid-works varies extremely; hardly ever falling below 2 per cent., it sometimes rises above 10 per cent. The latter, however, results from very bad work indeed; but 4 to 5 per cent. is considered very fair work; and as much is indeed required for the wet copper-extraction. The sulphur may even amount to 1½ times as much as the copper, but no more. At Oker the cinders are delivered to the extracting-works with 5 to 8 per cent. sulphur and 6 to 9 per cent. copper. If the pyrites arrives too well burnt from the acid-works, the copper-works add a little green pyrites in order to have sufficient sulphur for the first stage of their process.

The following analyses by Gibb show the composition of the pyrites-cinders as the copper-works receive them:—

	Rio-Tinto.	Tharsis.	San-Domingo.	Ytteroen (Norway).
Copper	1·65	1·50	1·55	1·01
* Iron	3·64	3·23	3·76	3·33
Sulphur	3·53	3·15	3·62	3·10
Cupric oxide	2·75	2·56	2·70	·39
Zinc oxide	2·02	·55	·47	6·46
Lead oxide	·47	·70	·84	·06
Silver	·0037	·0023	·0023	....
Cobaltic oxide	·007	·032	·033	....
Bismuth oxide	·013	·010	·013	....
Calcium oxide	·20	·25	·28	2·30
Ferric oxide	77·40	77·00	78·15	68·06
Sulphuric acid	6·10	5·25	5·80	6·56
Arsenic acid	·24	·17	·25	·05
Insoluble residue	1·45	5·85	1·85	8·74
	99·46	100·25	99·31	100·06

* Calculated as Cu_2S and Fe_2S_3.

Phillips states the following as the composition of cinders from San-Domingo ore:—

Sulphur	3·66
Arsenic	0·25
Iron	58·25(=83·0 Fe_2O_3)
Copper	4·14
Zinc	0·37
Cobalt	trace
Lead	1·24
Lime	0·25
Insoluble	1·06
Moisture	3·85
Oxygen and loss	26·93

Wedding and Ulrich found in samples from Widnes (*a*) and Hebburn (*b*):—

	Sulphur.		Copper.	
	a.	*b.*	*a.*	*b.*
Altogether	4·12	3·75	4·08	5·75
Of this soluble in water	43 p. c.	37 p. c.	46 p. c.	26·1 p. c.
" " " HCl	55	59	22·2	13·3
In the residue	2	4	31·8	60·6
	100	100	100	100

According to Hjelt the cinders from Spanish pyrites contai 0·19 per cent. arsenic.

The Oker cinders showed, on an average of a month's work:–

Copper (principally as CuO)	7 83 p. c.
Iron (principally as Fe_2O_3)	40·53
Lead (as PbO)	2·09
Silver	0·008
Zinc (as ZnO)	1·95
Manganese (as Mn_3O_4)	0·40
Sulphur	3·80
Sulphuric acid (corresp. to 3·8 S)	9·51
Alumina	4·43
Other gangue	11·65

The sulphur must be mostly in combination with iron, sinc unburnt crude ore could be seen as cores on breaking up the lump The sulphuric acid is partly combined with lime, partly wit metals, probably, as may be inferred from the well-known pr cesses of roasting, in the first line with CuO and ZnO, in th second line with FeO or Fe_2O_3. From this the following wou appear to be the most probable composition of the cinders:—

CuO	9·80 p. c.	
Fe_2O_3	53·14	(=37·2 Fe)
FeS_2	7·13	(= 3·8 S)
PbO	2·25	
Ag	0·008	
ZnO	2·43	
Mn_3O_4	0·57	
SO_3	9·51	
Al_2O_3	4·43	
Other gangue	11·65	
	100·918	

These cinders were formerly utilized in small blast-furnaces 7 ft. high, the first smelting yielding a rich coarse metal (55 per cent and a little blister-copper. Higher furnaces could not be used, o account of the large percentage of Fe_2O_3, which would have be partly reduced. The drawbacks of this smelting were the shor duration of the furnace-lining (47 to 72 hours), and great lo of metal by the slag and the flue-dust. Therefore, instead o smelting them, the cinders have latterly been worked up by the wet process.

The cinders are first *finely ground,* either by crushing-rollers or by edge-runners, and at the same time mixed with a sufficient quantity of *sodium chloride,* usually in its cheapest form, viz. rock-salt. This addition, where the furnaces are worked by hand, varies from 10 to 20 per cent., on an average it is 15 per cent. But with the mechanical furnace (p. 1129) only 7½ salt per cent. of burnt ore is required. The ground mixture is passed through a cylindrical sieve with 8 holes to the inch; the coarse particles are sent back to the mill, where they are ground down completely, so that the mixture always remains the same. The whole being finely ground, it is filled into old bogies and run on tramways over the calcining surfaces.

At Oker the cinders are mixed with 15 per cent. (formerly 20 per cent.) of Stassfurt potash salts (carnallite), and are ground down to the size of 2 millims. The Stassfurt salts contain the chlorides of magnesium, potassium, sodium, and calcium, all of which assist in the calcining-process.

Clemmer points out that, if the whole amount of cinder is ground to one size, this may cause difficulties. If too fine, a slimy mass will be formed in the tanks, which hinders the leaching-process; if too coarse, the chloridizing-process and the time of leaching are too much prolonged. It is best to grind one-third to pass through a sieve ⅛-inch mesh, and the remaining two-thirds quite fine, delivering the entire product to the furnace mixed with the salt in the mill itself. About one shovelful of salt is allowed to six of cinders.

The *calcination* or *roasting* takes place in furnaces of very different kinds. These may be classed as follows:—

1. *Ordinary reverberatory furnaces,* similar to black-ash furnaces. These were in use at first, but have been given up long since.

2. *Reverberatory furnaces with gaseous fuel.* These are principally used in Lancashire; they are illustrated by figs. 471 and 472.

Three gas-producers furnish the gas for eight calcining-furnaces; it passes from the main flue into the flue E across the width of the furnace; from this it rises through 5 vertical flues G, each of them provided with a damper; it then travels through the flues F below the furnace-bed, then directly over the charge and through the outlet M to the condensers. The air for combustion is introduced by two tiers of holes with slides in each of the two furnace-ends

Fig. 471.

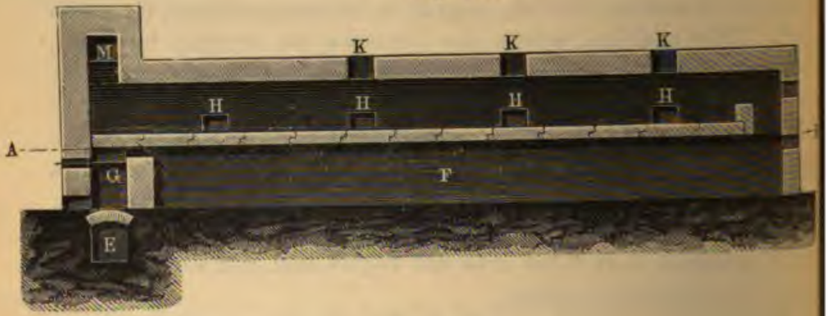


Fig. 472.

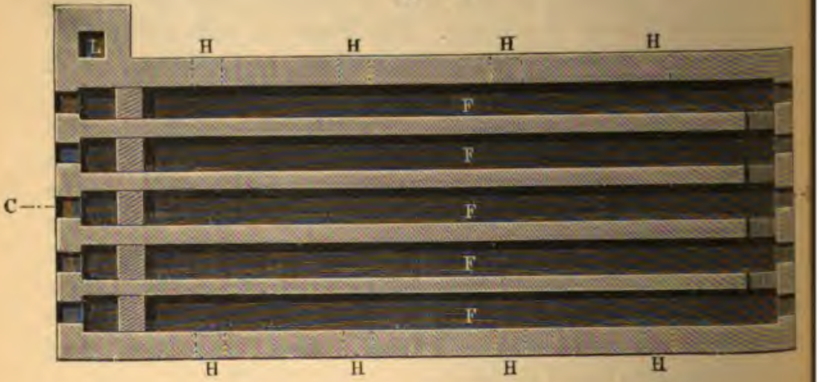


Fig. 473.

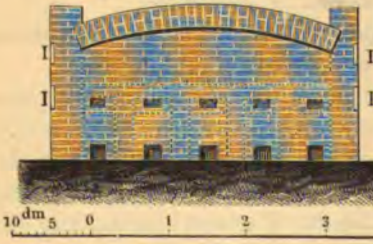
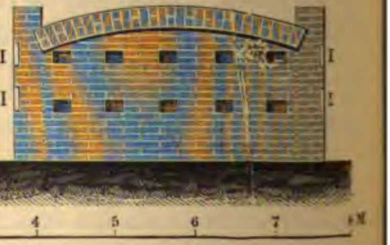


Fig. 474.



(figs. 473 & 474), so that one of the tiers communicates with the flues below the bed, the other with the space above the fire-bridge.

Thus the combustion can be regulated so that some unburnt gas gets as far as the fire-bridge and is only lighted there. H H are the working-doors; K, charging-holes in the arch, closed by loose

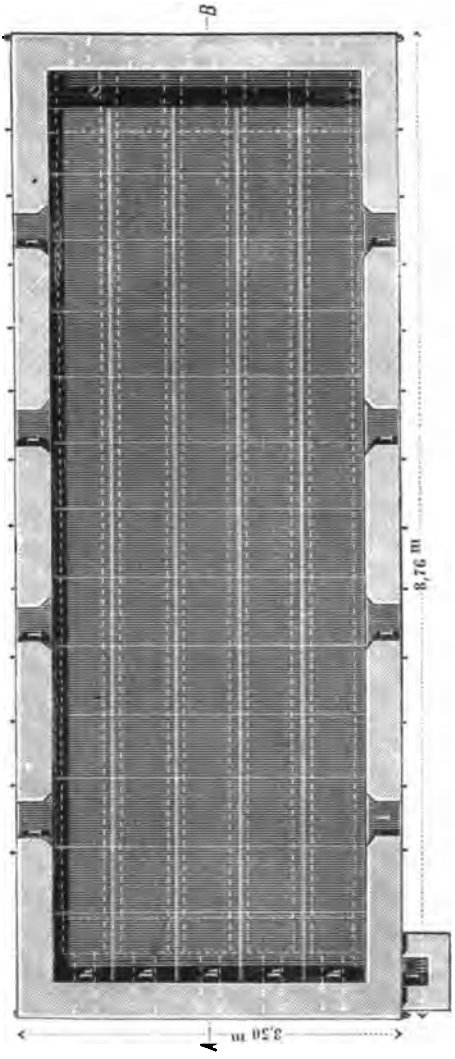


Fig. 475.

metal plates and fine ore on the top of these; I, binding-plates. Each furnace holds 45 cwt. of ore.

Similar furnaces are used at Oker; these are represented in figs. 475 to 478. They work two charges of 2½ tons each every

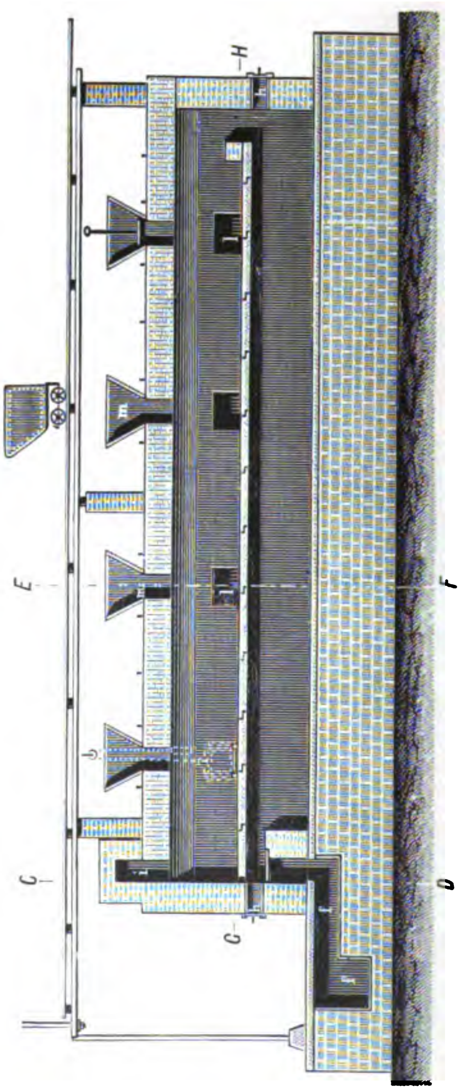


Fig. 476.

24 hours. Here *f* marks the main channel for the gas; five channels for the same below the furnace-beds; *h*, the slits

Fig. 477.

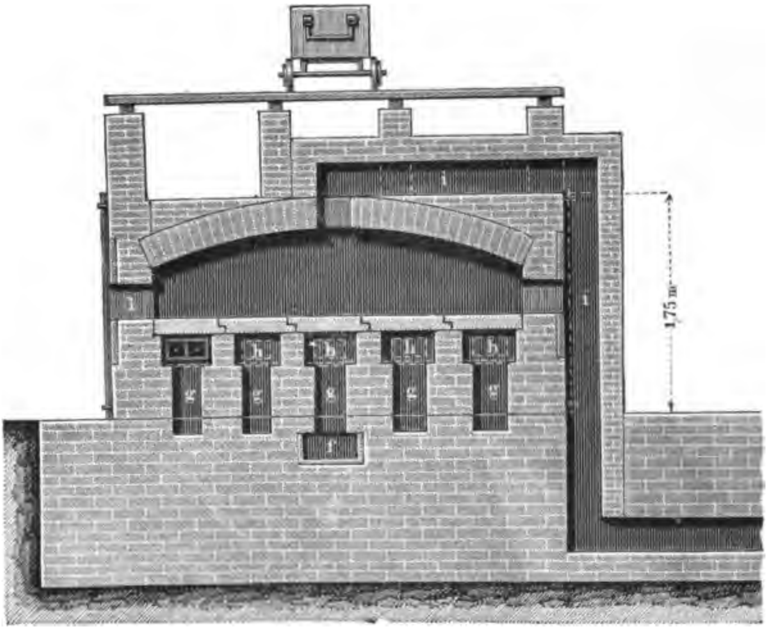
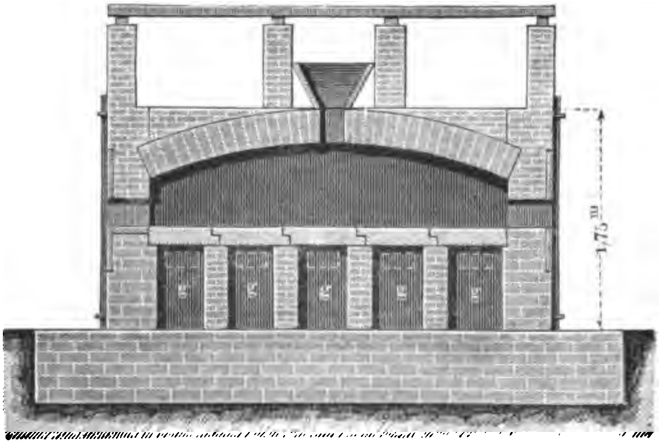


Fig. 478.



introducing the air ; *i*, the outlet for the mixed fire- and calcining-gas to the condenser; *l*, the working-holes ; *m*, the charging-hopper.

3. *Blind roasters* (muffles), employed at all the works of the Tharsis Sulphur and Copper Co., figs. 479 to 481. Here the flame does not come into direct contact with the charge, but only acts through the brickwork of the bed and the arch. The charge is worked in the muffle G, with the working- and discharging-doors M. Its bottom is formed by fire-clay slabs covering the fire-flues V L ; its cover by a thin arch. The ore is spread in a thin layer, and receives the air necessary for its roasting only through the working-doors M ; in the other part of the furnace the oxygen contained in the fire-gas is active as well. The flame from the double grate H first travels by I over the muffle-arch, then downwards in three channels on each side (V_2 & V_2'). The gas of each three channels is united in a flue (L & L′), and, after having returned in the opposite direction, descends by *m* into the flue *n* situated below the ground-line, which enters the main chimney. *o* is the regulating damper; *p*, the outlet for the calcining-gas, which descends by *r* to the horizontal subterraneous flue *q*, and thence arrives at the acid-condensers. The metal dish N, on the top of the furnace, serves for a first heating of the mixture; it communicates with the muffle through several pipes usually covered with a metal plate; by raising the latter the mixture is let down into the muffle.

The muffle-furnaces at Natrona are exactly similar to the above. We therefore abstain from reproducing the design in Min. Ind. ix. p. 287, and merely quote the dimensions of those furnaces. Ash-pit 18 in. wide, 3 ft. 1½ in. deep. Fire-grate 18 in. × 9 ft. Fire-bridge 2 ft. 6 in. from grates to top of muffle-arch. Space between top of muffle-arch and bottom of outer arch 14 in. (The first 6 feet of the muffle-arch are double, the remainder only ½ brick. Width of furnace-hearth 10 ft. from door to door, 7 ft. 9 in. clear (each side wall being 13½ in. thick) ; length 35 ft. clear ; height 18 in. to spring, 30 in. to crown of arch. Pillars to support hearth 16½ in. wide, 20 in. apart. Four charging-hoppers, 18 in. wide; one cast-iron gas-pipe passing through both arches, 9 in. wide.

Muffle-furnaces seem to have superseded at present all other descriptions of calcining-furnaces for this purpose.

Fig. 479.

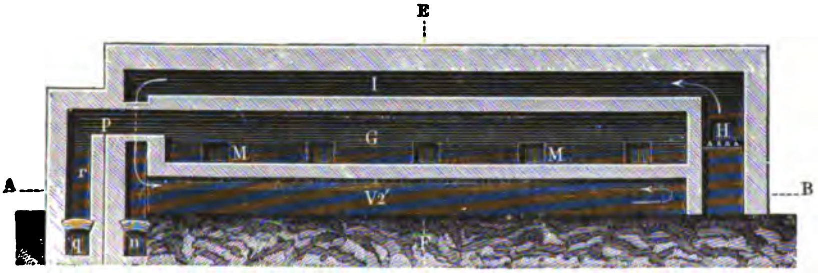


Fig. 480.

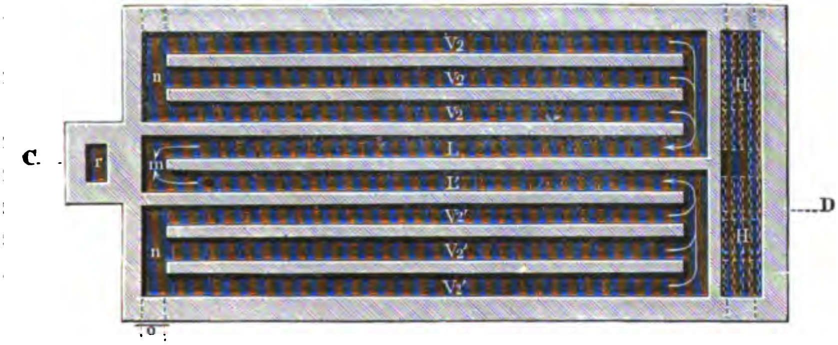


Fig. 481.

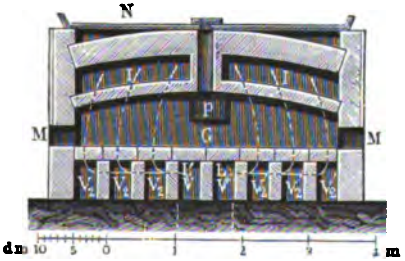


Fig. 482.

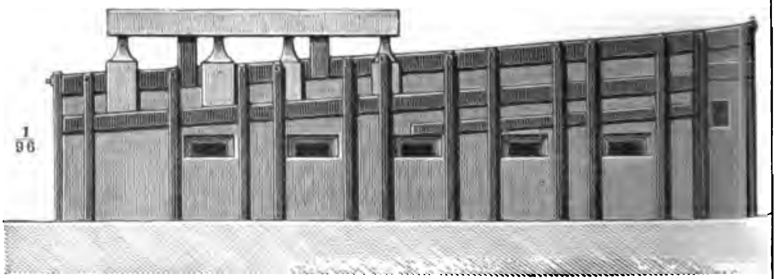


Fig. 483.

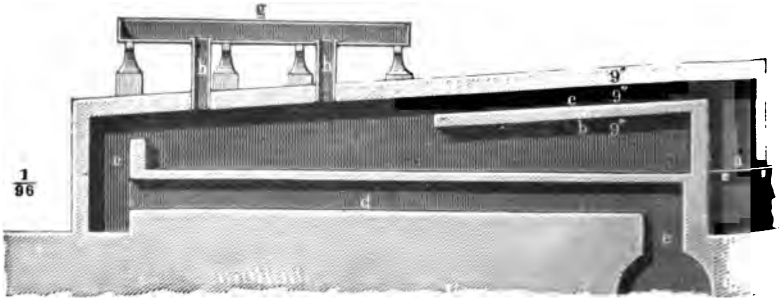
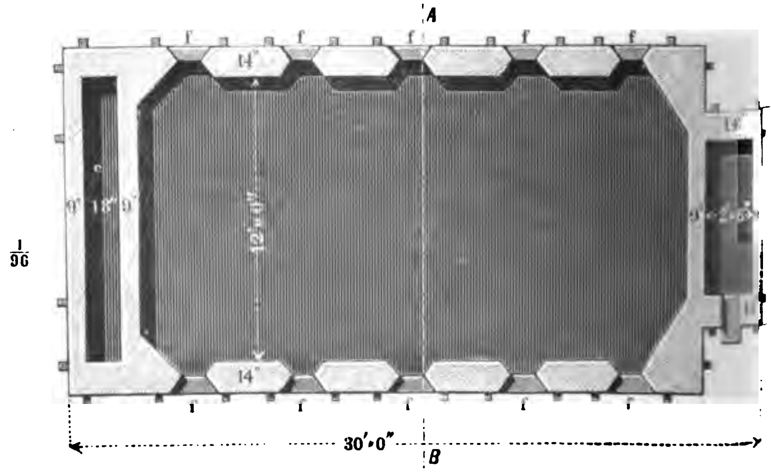
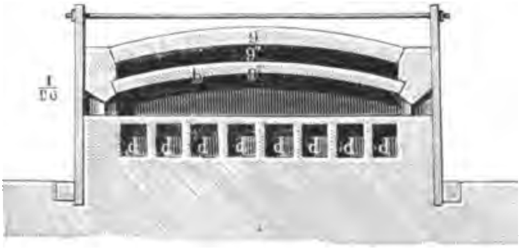


Fig. 484.



4. *Combined furnaces,* used by the Bede Metal Company at Hebburn-on-Tyne (shown in figs. 482 to 485). Here the flame of the fire, *a,* does not play direct upon the charge, but is kept off it by an arch, *b,* reaching half the length of the furnace; after this the flame touches the furnace-bed directly and descends by *c* in order to return by eight channels, *d d,* beneath the furnace-bed, and to escape at *e* into an underground flue leading to an acid-condenser. The working-doors *f f'* serve for stirring and discharging; the pan *g* for a first heating of the charge; the pipes *h h* for dropping it into the furnace. The purpose of the arch *b* is to avoid overheating those portions of the ore nearest the fire-bridge, in which the copper might easily be roasted dead; in fact the hottest part of these furnaces is that behind, the part below the protecting arch hardly attaining a dark red-heat.

Fig. 485.



5. *Mechanical calcining-furnaces* with revolving hearth, patented in 1872 by Gibb and Gelstharpe, and 12 of which exist at the Bede metal-works. Figs. 486 to 489 represent this furnace. The bed consists of a circular pan, *b b,* made of boiler-plate, lined with fire-bricks, D. The side walls, *m m,* and the arch, *n,* form the other parts of the calcining-space. On one side there is a fire-place, C, whose flame travels across the hearth to F, whence it enters an underground flue leading to the chimney, along with the gas evolved in calcining. The pan *b b* is carried on wrought-iron girders fixed on a central cast-iron spindle which works in a foot-step and is maintained in a vertical position by a collar, fitted with brasses, in which an upper bearing of the spindle works, carried by the tubular cast-iron stays *g g.* This pan is caused to revolve in its own plane on the central footstep by an endless

Fig. 486.

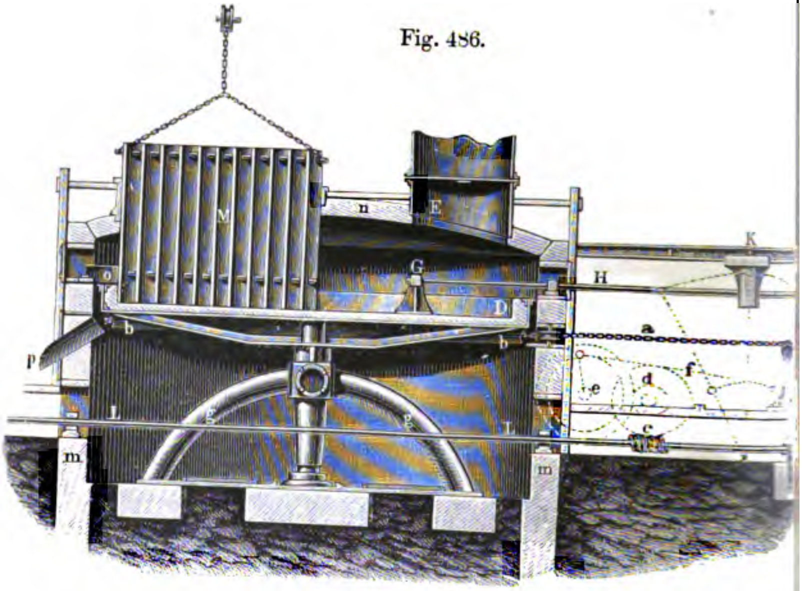


Fig. 487.

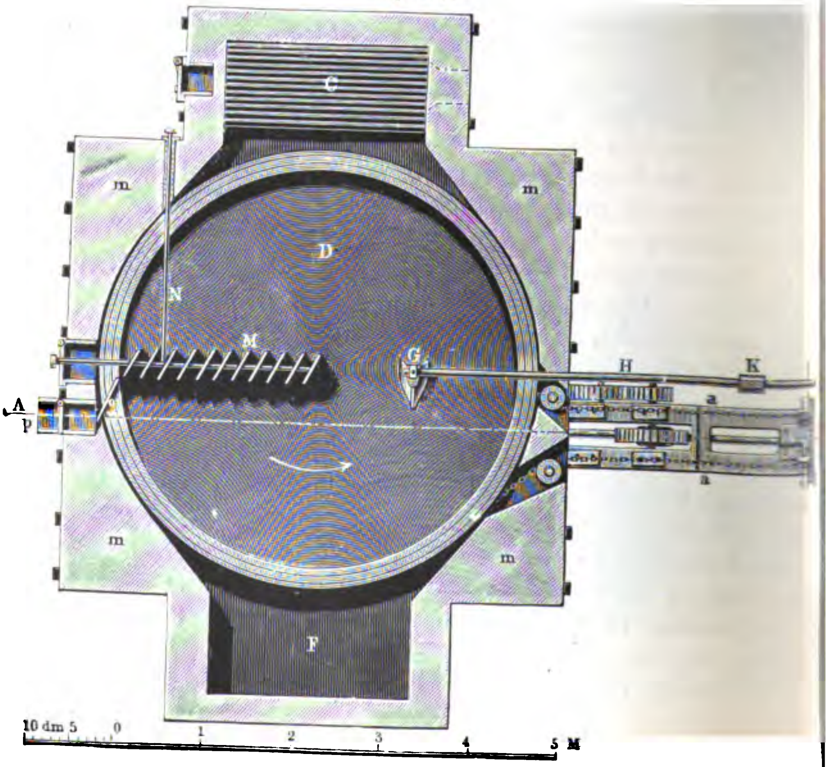


Fig. 488.

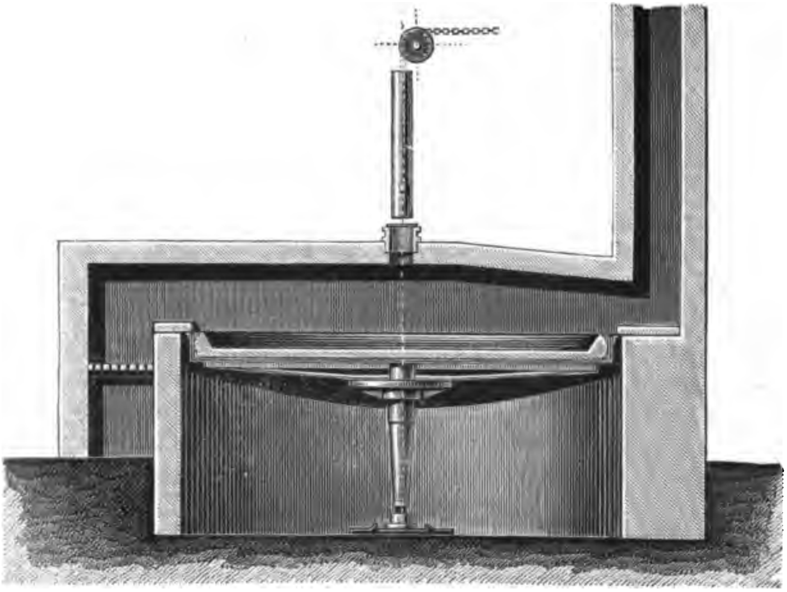
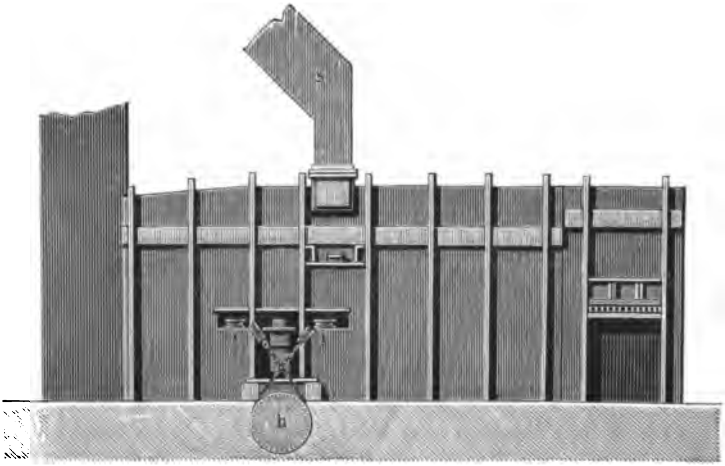


Fig. 489.



chain, *a*, carried round a sheave, I, from which it passes over the guiding-pulleys *i i* to the horizontal sheave underneath the pan.

A small pump, driven by the same main shaft, constantly pump lubricating-oil from a tin vessel into the footstep, the excess of oil running back into the same vessel again. The hearth is traversed by a cast-iron plough, G, made to reciprocate in a radial line o the circle by the wrought-iron arm H connected with the cross-head K. The motion of this cross-head is equal to the radiu of the hearth, and is derived from the driving-shaft L by means o the worm and scroll-wheel *c* and the pair of spur-wheels *d* and the larger of which, by means of the crank-pin and connecting-rod *f*, gives a reciprocating motion to a lever, the forked uppe end of which, by means of pins working in slots, moves th cross-head with the plough-arm and plough. The speeds o the circular hearth and the plough are so adjusted that th plough does not travel more than its own breadth during one revolution of the hearth; so that every part of the circle of th hearth is gone over by the plough in each journey from or to it centre.

The furnace is charged by means of the hopper E, let into slit of the arch, and discharged by a set of parallel plates M, which are arranged obliquely across a radial line of the circle o the hearth on the opposite side of the centre to that in which th plough travels. These plates are rigidly bound together at to and bottom, and suspended by a chain, so that they can be raise out of or lowered into the furnace through the roof. The plate are shown in the furnace in the position for discharging, with plate, *o*, fixed in the doorway, folded against the outer plate of th series M. When the discharging-plates are in this position, eac throws the ore carried against it by the revolution of the heart towards the circumference into the path of the next outward plat by which it is again thrown outwards at the next revolution, to b at length propelled against the doorway-plate *o*, which throws from the edge of the hearth on a shoot, *p*, over which it runs o to the floor outside the furnace. When the furnace is workin the plates are raised through the roof, and the opening throu which they pass is closed by a slide. The bolt N fixes the plate in their position.

In order that the pan may freely revolve round the spindle, th side walls *m m* are 1 inch apart from the edge of the pan; th air rising in this intermediate space causes the oxidation. The brickwork reaches down to the ground-line; and the machinery underneath the hearth is only accessible by an iron door, so that it is protected from the coal- and ore-dust. Every part of the machinery is very strong and not liable to get out of repair—excepting the cast-iron plough, G, which must be replaced once a fortnight, but at a smaller expense than that of the tools in a furnace worked by hand. The plates M suffer very little, because they are only for a very short time exposed to the fire. The twelve furnaces at the Bede metal-works are driven by two steam-engines of 18 indicated horse-power each.

All these different descriptions of furnaces have the same object; and the *style of working* is accordingly very similar in all cases. The ore must, of course, be completely roasted—that is, sufficiently to convert the copper into sulphate, which, owing to the presence of sodium chloride, at once forms with this, by mutual decomposition, cupric chloride and sodium sulphate; whilst the iron should be converted as completely as possible into ferric oxide, so as to become insoluble. In this process, owing to the simultaneous action of SO_3 and O upon NaCl, chlorine is evolved, which must greatly aid in chlorinating the copper as well as any other metal present. At the same time a large quantity of HCl is formed, which converts the oxides of copper, silver, zinc, &c. into chlorides, whilst at the calcining-temperature ferric chloride cannot continue to exist as such. At Oker the formation of hydrochloric acid is purposely aided by using carnallite in lieu of common salt, as the $MgCl_2$ contained in the former readily yields MgO and HCl. This, however, is not absolutely requisite, as with 2NaCl the $CuSO_4$ already produced in calcining yields $CuCl_2$ and Na_2SO_4. Cu_2Cl_2 also is always formed at the same time. Since the chlorides of copper are both unstable and volatile at very high temperatures, a low red-heat ought not to be exceeded; so that any copper-pyrites still present in the cinders is not burnt, and therefore escapes chlorination. Accordingly, copper-pyrites (or Cu_2S) ought not to be present in any quantity for the wet-extraction process; and consequently ores with more than 8 per cent. of copper, which can never be roasted with sufficient completeness in the chemical factories, cannot be utilized by this process, but only by smelting.

Manifold experience has taught that without employing common salt (that is, without chlorinating) it is never possible, even approximately, to hit the point where the more easily decomposed ferric sulphate no longer exists, whilst the less easily decomposable cupric sulphate is still present as such, the iron being then present in an insoluble, the copper in a soluble form. If ferric salt remains in a soluble form, it naturally passes over into the lyes, and, in the operation of precipitating the copper, causes a great loss of metallic iron by its reduction to ferrous salts. If, on the other hand, much copper has likewise passed into an insoluble form. more hydrochloric acid is required for its solution. In any case the formation of some cupric oxide and cuprous chloride, insoluble in water, cannot be avoided.

Wedding has observed, and described in detail, the calcining-process as carried on at Widnes in a gas-furnace. The charge, of 45 cwt. of ore mixed with 17 per cent. of salt, is let down on to the hearth, spread out and slowly heated till a low red-heat has been reached nearest the fire-bridge; the charge is turned over and left to itself, the gas being shut off, but the air being allowed to enter, so that after two hours scarcely any glowing can be perceived at the fire-bridge. After one hour's and three hours' calcining respectively, the copper of the charge behaved as follows:—

	1 hour's calcining. per cent.	3 hours' calcining. per cent.
Soluble in water	54	51
„ HCl	38	42
„ NO_3H	8	7

After three hours the charge is quite dark, and is now well turned over with a slice of 3 or 4 inches breadth, as well as with a rake; there ought to be no necessity for giving more fire, as the temperature should from the first have been raised to the proper point. On raking over the charge, which is now done regularly with short interruptions only, the temperature rises of itself in consequence of the chemical reactions, the rise becoming sensible after 4¾ hours (counting from the beginning); so that after 5¼ hours a dark red-heat has been reached. Up to this point there is a copious evolution of white vapours and blue flames; from this period there is less of these, and it is the calciner's principal task to see that the heating of the charge is quite equal all over, and that some places do not show more blue flames than others. After

6½ hours these flames almost entirely disappear; and this fact, along with the greenish-grey colour of the charge, constitute the practical tests for judging whether the operation is finished. A sample is now drawn; and if its examination shows the completion of the calcining-process, the charge, which has now been 6½ or 6¾ hours in the furnace, is drawn out. Of the copper now

75 per cent. is soluble in water,
20 „ „ HCl,
5 „ „ NO_3H.

Good workmen can finish the calcining in a gas-furnace in six hours.

Wedding observes that the watery solutions constantly show more sulphur, and that the testing of the calcined ore of different works proves the process to be carried out very unequally; but it is certain that the best results are in fact got by the most careful work. The calciner's task is, first to heat the charge and thus to start the chemical reactions, but then to maintain these at the lowest possible heat up to the finish, and to spread them equally through the whole mass. It is of great importance not to leave the ore any longer in the furnace than exactly the necessary time; this is made difficult by the depth of the layer of ore, viz. 5 or 6 inches—which, on the other hand, facilitates the chlorination, since the gas rising in the ore heated both at top and bottom has all the more opportunity of coming into contact with all parts of it.

Evidently the process is altogether dependent upon the skill of the workman, whilst with the mechanical furnace of Gibb and Gelstharpe only the firing needs attention. In the latter furnace indeed a lower heat is sufficient, one that never reaches a red glow visible in daylight.

At Oker, where gas-furnaces exactly like those of Widnes are used, each charge of 50 cwt. of ore with 15 per cent. potash salts is brought to a low red-heat in four hours; the firing is then interrupted and the mass raked over. Owing to the chemical reactions, the heat at first increases, but towards the end goes back again. During the turning-over stage, which lasts five hours, the air-slides are opened to admit the air to the charge; after that time the charge is drawn. Two charges are put in every 24 hours.

Analysis of a sample taken in the middle of the calcining-process (the mixture containing 20 per cent. carnallite):—

Soluble in water.

	per cent.			per cent.
Cu	1·94,	calc. as	$CuCl_2$	3·11
Ag	0·003,	„	AgCl	0·004
Fe	0·74,	„	$FeCl_2$	1·68
Al_2O_3	0·11,	„	$Al_2(SO_4)_3$	0·39
Mn	0·69,	„	$MnCl_2$	1·58
Ni	0·20,	„	$NiCl_2$	0·44
Zn	1·60,	„	$ZnCl_2$	3·40
CaO	2·76,	„	$CaCl_2$	6·27
MgO K_2O Na_2O		„	Sulphates	18·15
				35·024

Insoluble in water.

	per cent.			per cent.
Cu	4·32,	calc. as	CuO sol. in HCl	[illegible]
			Cu_2S sol. in aqua regia	[illegible]
Pb	0·39,	„	$PbSO_4$	[illegible]
Fe	34·49,	„	Fe_2O_3	[illegible]
			$Fe_2(SO_4)_3$	[illegible]
			FeS_2	[illegible]
Al_2O_3	3·30,	„	Al_2O_3	[illegible]
Mn	0·03,	„	Mn_2O_3	[illegible]
Zn+Ni	0·29,	„	ZNO+NiO	[illegible]
CaO	0·45,	„	$CaSO_4$	[illegible]
SO_3	1·86			
S	1·47			
Cl	trace.			
Insoluble in acids				[illegible]
				[illegible]

Sample of calcined ore taken at the finish:—

Soluble in water.

	per cent.			per cent.
Cu	3·86,	calc. as	$CuCl_2$	8·17
Ag	0·005,	„	AgCl	0·006
Fe	0·60,	„	$FeCl_2$	1·38
Al_2O_3	0·17,	„	$Al_2(SO_4)_3$	0·56
Zn	1·64,	„	$ZnCl_2$	3·42
Mn	0·75,	„	$MnCl_2$	1·71
Ni	0·07,	„	$NiCl_2$	0·15
CaO	1·60,	„	$CaCl_2$	3·17
MgO K_2O Na_2O		„	Sulphates	20·50
				39·066

Insoluble in water.

	per cent.			per cent.
Cu	2·57,	calc. as	CuO	[illegible]
			Cu_2S	[illegible]
Pb	1·17,	„	$PbSO_4$	[illegible]
Fe	34·56,	„	Fe_2O_3	[illegible]
			$Fe_2(SO_4)_3$	[illegible]
			FeS_2	[illegible]
Al_2O_3	0·44,	„	Al_2O_3	[illegible]
Zn	0·37,	„	ZnO	[illegible]
Mn+Ni	trace.			
CaO	0·49,	„	$CaSO_4$	[illegible]
SO_3	1·49			
Cl	trace.			
S	0·64			
Insoluble in acids				[illegible]
				[illegible]

The mechanical furnace has the advantage also in respect of the addition of salt; only 7½ per cent. of salt is required in it, against 15 in the hand-furnaces. Often only a portion of the salt is mixed with the ore at the outset, and the remainder added afterwards. In the blind roasters the ore is calcined first nine hours with 1[illegible] per cent. salt, and another three hours with 8 per cent. more salt. In the combined furnaces with protecting arch the weight of ore is 58 cwt., and the time of calcining eight hours; in the mechanical furnaces 5 tons and nine hours.

Gibb gives the following analyses of the results of calcination:—

	Gas-Furnace.		Close Furnace.		Mechanical Furnace.	
	p. c.	Cu p. c.	p. c.	Cu p. c.	p. c.	Cu p. c.
Cupric chloride ...	4·03	= 1·90	4·25	= 2·00	6·70	= 3·15
Cuprous chloride ...	·32	= ·20	·35	= ·21	nil.	
Cupric oxide.........	1·26	= 1·00	·88	= ·70	·32	= ·25
Sodium sulphate ...	2·50		3·40		0·90	
Insoluble copper ...	13·18		17·40		14·03	
		·15		·12		·13
Total copper......		3·25		3·03		3·53

The principal point is always this, that as little copper as possible should remain in a state insoluble in water and dilute acids. In the above cases the quantity varies from 0·12 to 0·15 per cent.; the slightly more favourable result of the blind roaster, according to Gibb, is far more than counterbalanced by its greater consumption of fuel (50–100 per cent.). The most favourable result is obtained with the mechanical furnace, in which next to no cuprous chloride and, even with the worst ores, rarely more than 0·25 per cent. of CuO are formed.

At Oker the average result of the constantly taken samples of calcined ore is: 75 per cent. of the copper contained in the ore is soluble in water, 20 per cent. in dilute hydrochloric acid, and 5 per cent. in aqua regia.

If the pyrites contains more than 4 per cent. copper, the cinders cannot be worked in England with advantage by the wet process. At the Bede metal-works many experiments have been made with richer ores: but with 6 per cent. copper the salt, the coals, and the labour are too dear. In this case, however, another circumstance comes into play: by the Cornish copper assay about 2 per cent. copper less than the truth is indicated; and this with a poor ore of course amounts to a much larger proportion of the whole (sometimes more than half) than with richer ores; thus the former are cheaper for the wet process than the latter. At Oker, where this reason does not exist, ore up to 8 per cent. Cu can be extracted by the wet process.

It has already been remarked that the sulphur in the cinders must bear a certain proportion to the copper; with a 4-per-cent ore it ought not to exceed 6 per cent.; an equal percentage of S and Cu is preferable. If less S is present, raw pyrites must be added. The more S there is present, the more salt must be added, and the more time will the calcination take.

The *tests* for ascertaining the completion of the calcination are of a very simple character, which is the more necessary as they must be made very quickly. A certain measure of the charge, not weighed, is lixiviated by water and dilute HCl, just as on the large scale; the residue is boiled with aqua regia, supersaturated with ammonia, and allowed to settle; the more or less blue colour of the solution of ammonio-cupric salt gives a sufficient indication of the percentage of insoluble copper.

Condensation of the calcination-gas.—In all the descriptions of furnaces mentioned above, except the blind roasters, this gas is mixed with the fire-gas, but even in these it is mixed with air to such an extent that a condensation of strong acid is not very well possible. The acid is a little more concentrated than that from open calciners; but this matters very little, as it is always used in a very dilute state for lixiviating. The calcination-gas principally contains (besides oxygen and nitrogen) SO_2, SO_3, HCl, Cl, and very small quantities of metallic chlorides. Henderson had proposed to volatilize the copper entirely as $CuCl_2$, and condense the latter in towers; but this has turned out quite impracticable. The small quantity of copper passing over into the condensers, about $\frac{1}{4}$ per cent. of the whole, is not lost, as the condensed acid is used for lixiviating the charge.

The condensation of the gas from the calciners takes place in towers of exactly the same kind as those (described in detail in the second volume) for hydrochloric acid—that is to say, made of brickwork set in tar and sand (or, better, of stone flags), and packed with coke, fire-bricks, and the like. Sometimes condensers made of very large stoneware pipes are employed. A coke packing can be used with blind roasters; but the other furnaces require a packing of bricks or stoneware, and must have larger condensers, as these have to serve for a larger volume of gas. The size of the towers varies with that of the plant; for 12 furnaces a tower of

8 feet square and 40 to 50 feet high is sufficient. The gas enters at the bottom, meets a spray of water coming from the top, which washes the acids out of it, and again leaves the tower at the top, whence it is taken downwards into a flue leading into the chimney.

The total condensed liquid (a mixture of weak sulphuric and hydrochloric acids; the SO_2 in the condensation is oxidized to SO_4H_2 by the action of the chlorine) is used in the succeeding operation of lixiviating, and frequently is not even sufficient for dissolving all the CuO and Cu_2Cl_2.

Lixiviation of the calcined mixture.—The mixture is carried in bogies running on tramways over each of the lixiviating-tanks and tipped into these. The only available material for the tanks is wood; most metals are excluded by the nature of the lixiviating-liquid; stone, asphalt, &c., both by their costliness and by the heat of the charge. As such large wooden vessels cannot well be kept tight on account of the unavoidably rough treatment and the hot acid liquors, the whole floor of the lixiviating-shed is covered with a thick layer of asphalt and slopes to one side, so that all liquors leaking out run off to a catch-well, into which enter at the same time earthenware spouts for carrying the strong copper-liquors.

The lixiviating-tanks are square, about 11 × 11 feet wide and 4 to 5 feet deep, made of well-seasoned and planed 3-inch planks, kept together by corner-pieces, screw-bolts, &c. The joints are tightened by putting on a little red-lead before putting the planks together; the bottom joints are besides caulked with tarred spun yarn, and the whole vessel painted with hot coal-tar. At Oker lead-lined vessels are used, which are very expensive and frequently need repair. On the bottom, laths on end are placed; upon these, perforated fire-tiles or boards; upon this false bottom a layer of sifted furnace-cinders is spread out; and on the top a layer of heather or coke (at Oker of straw) 3 to 6 inches deep is put. The liquors are conveyed in earthenware and india-rubber tubes of 3 to 4 inches diameter, the latter provided with iron pinch-clamps. In order to force the liquors from one tank to the other, or from the catch-well into the tanks, simple stoneware injectors are provided. Each tank has a steam-pipe for heating.

At Natrona the leaching- and precipitating-tanks are made of very sappy yellow pine, well tarred before use, and consist of an outer shell of 3-in. planks, an inner lining of the same thickness, leaving a 3-inch space between the two layers of timber, which space is afterwards filled with a mixture of "hard tar" (probably soft pitch) and screened sand, melted together in a kettle and wel mixed before pouring in. The bottom is covered with a 3-inch coat of the same material. The planks are put together with wooden pins and bound, as shown in fig. 490. The ends or joi are halved together, and caulked with oakum and red-lead. Th

Fig. 490.

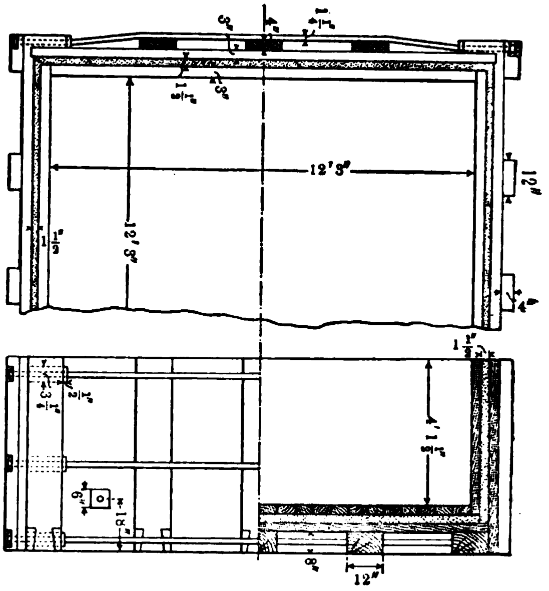
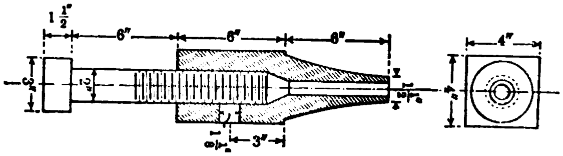


Fig. 491.



tanks are 12 × 12 ft., 4 ft. or 6 ft. deep. In lieu of a grating, hard-burned bricks are laid flat side by side. Fig. 491 shows the wooden spigot serving in lieu of an outlet-cock.

Into each tank about 10 tons of calcined ore are put, quite hot from the furnaces, and are first covered with weak liquor from a previous operation, which gets heated by the heat of the mass itself. After one or two hours the now concentrated liquor is run off by a plug-hole below the false bottom, and goes forward to the precipitation. The plug is put in again, and the lixiviation continued by hot water; thus weaker liquors are produced, which are forced to a fresh tank as just described. Generally three waters are put on, and thus most of the purest copper and 95 per cent. of all the silver contained in the pyrites are obtained. Then follow several (up to 6) washings with the weak condenser-acid, or, if this does not suffice, with hydrochloric acid bought for the purpose and much diluted. This is not necessary with mechanical furnaces, because the copper-salts from these are mostly soluble in water; but it is generally necessary with hand-furnaces. Even when no acid need be bought, but sufficient condenser-acid is obtainable, a saving of acid is important, since the condenser-acid conveys arsenic and bismuth into the copper.

The liquors obtained by the use of acid contain many impurities, especially As, Bi, Sb, and Pb—according to Gibb, for each 100 parts of Cu, 5·4 As and 0·3 Bi; and they are accordingly treated separately in most works, because they yield impure copper.

It is a principal rule to allow each water to stand only a few hours on the ore; the nine washings of each tank, together with charging and emptying it, are not to last beyond 48 hours. Accordingly, for each 5 tons of calcined ore obtained per diem one tank is required, and besides, on the whole, a few reserve tanks.

The residue from lixiviation, after draining, is tipped on a heap and afterwards sold to the iron-smelters. It is the value of this residue which makes the wet process in this case more profitable than the dry process, as it forms a valuable iron-ore, going by the name of "purple ore" or "blue billy." The following is the composition of two average samples:—

Ferric oxide	90·61	95·10
Copper	0·15	0·18
Sulphur	0·08	0·07
Phosphorus	0	—
Lead sulphate	1·46	1·29
Calcium sulphate	0·37	0·49
Sodium sulphate	0·37	0·29
Sodium chloride	0·28	—
Insoluble	6·30	2·13
	99·62	99·55
Metallic iron	63·42	66·57

This ore is thus shown to be very rich in iron, entirely free from phosphorus, and to contain very little sulphur; its slight percentage of copper does no harm. The only drawback is its fine state of division. It can to some extent be employed directly in its pulverulent state as a mixture with 5 or even only 3 parts of lump iron-ore in blast-furnaces; using limestone in addition, both grey and white pig can be made from it. Most of this ore, however, is used for "fettling" the sides and bottom of puddling-furnaces in lieu of hæmatite, for which it is very well adapted, or in the Siemens-Martin process. Its direct conversion into iron and steel on the large scale has not yet been carried out. At Oker it is easily used up in the various metallurgical processes there carried on, and even its small percentage of copper is turned to account. They obtain upon 130 parts of pyrites-cinders, 75 parts of extraction residues of the following composition:—

Ferric oxide	79	per cent.
Alumina	3	„
Magnesia and alkalies	1	„
Lime	2·5	„
Sulphuric acid	5·5	„
Insoluble in acids	6	„

Purple ore is more valued the freer it is from siliceous gangue; and for this reason that made from Spanish and Portuguese is preferred to that from Norwegian pyrites.

According to Clemmer (Min. Ind. ix. p. 289) the purple ore is now moulded in America into briquettes (it is not stated with what agglomerating substances) by an ordinary automatic brick-making machine and burned in a down-draught kiln. These briquettes test less than 0·25 per cent. sulphur, and are easily disposed of to pig-iron manufacturers, some of whom require all the sulphur to be removed; for this purpose the briquettes must be burned at a very high temperature for five or six days and virtually fused.

Comp. p. 1105 as to the various processes for agglomerating pyrites-cinders, all of which of course apply also to purple ore.

The *lead* contained in the pyrites exists in the cinders as sulphate. Part of this is carried away with the leaching-liquors in the shape of mud and is removed by settling out; this mud contains some gold. Another portion remains behind in the lixiviated residue, mixed with the purple ore and injuring its quality as an iron-ore.

Schaffner (Fischer's Jahresb. 1880, p. 136) removes and utilizes the lead in the following simple and cheap manner:—After roasting the ore with common salt as usual and washing out all soluble chlorides and sulphates, the residue is drenched with chloride-of-calcium liquor (from the Weldon chlorine process) of 9°–12° Tw., heated to about 40° C., and acidulated with hydrochloric acid. By mutual decomposition gypsum and lead chloride are at once formed, which remain *dissolved* in the acid liquor. This is run off and brought into contact with metallic iron, which precipitates the lead in the metallic state. After washing, the purple ore is quite free from lead sulphate. At the same time the $CaCl_2$ dissolves the last traces of copper and silver present as Cu_2Cl_2 and $AgCl$; these are precipitated along with the lead. It should be noticed that sulphuretted hydrogen fails to indicate the lead in a solution of $PbCl_2$ in $CaCl_2$ acidulated with HCl.

Where the copper is precipitated by spongy iron, a portion of the purple ore is employed for preparing the latter.

Copper-liquor obtained by lixiviation.—The effect of the lixiviation is best seen from the following analyses by Gibb, which at the same time illustrate the great difference of work between mechanical and hand-worked furnaces:—

	Mechanical-Furnace Ore.		Hand-worked-Furnace Ore.	
	per cent.	Copper, per cent.	per cent.	Copper, per cent.
Soluble in Water:				
Cupric chloride	4·16	1·96	3·81	1·82
Cuprous chloride	none		·19	·12
Cupric sulphate	1·83	·81	none	
Ferrous sulphate	·15		none	
Ferric sulphate	·75		none	
Zinc sulphate	2·01		1·95	
Calcium sulphate	1·29		1·39	
Sodium sulphate	9·17		11·13	
Sodium chloride	none		2·64	
Soluble in dilute Hydrochloric Acid:—				
Cuprous chloride	·015	·01	·33	·21
Cupric oxide	·225	·18	1·01	·81
Lead sulphate Ferric oxide	not determined.		not determined.	
Residue (by difference):—				
"Purple iron-ore"	80·40	·08	77·55	·11
	100·00	3·04	100·00	3·07
Sodium chloride equivalent to sodium salts as above	7·56		11·81	

The composition of the copper-liquor, according to Gibb, is, in grams per litre:—

From hand-worked Furnaces.		From mechanical Furnaces.	
Sodium sulphate	144·1	Sodium sulphate	110·9
Sodium chloride	63·9	Sodium chloride	4·1
Chlorine in combination with heavy metals	67·1		
Copper	53·0	Cupreous chloride	53·2
		Cupric chloride	0·8
Zinc	6·9	Zinc sulphate	10·1
Lead	0·6	Lead sulphate	0·8
Iron	0·5	Ferrous sulphate	4·3
Calcium	0·7	Calcium sulphate	5·0
Silver	0·047	Silver	not estimated

At Oker the process was formerly carried out in the following way *. The calcined charge is lixiviated in parcels of 5 tons each first with the final liquor, which is always regenerated in the process. 100 parts of the latter, of 1·145 spec. grav., contained:—

	per cent.		per cent.
Cu	0·015	CoO + NiO	0·01
Pb	trace	CaO	0·12
FeO	2·14	MgO	0·52
Fe_2O_3	0·15	Alkalies	2·61
Al_2O_3	0·11	Cl	2·56
ZnO	0·06	SO_3	5·89
MnO	0·31	As + Sb	trace

Total solids...... 14·495 per cent.

This liquor, already heated in pumping by the injector to 50° C., is further heated, when it comes into contact with the calcined charge, by the solution of the anhydrous salts, of course also by the heat of the charge itself, nearly up to the boiling-point, by which the solution is assisted. When the charge is perfectly penetrated by the final liquor, the outlet-tap is opened and fresh final liquor runs in as long as the copper-liquor running away at the bottom still shows a blue colour. This first period lasts four

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* This process is still described here, as it may be of use in analogous cases; but it has now been discontinued at Oker, the character of the copper-ores having changed, so that they cannot be subjected to the wet-extraction process.

or five hours, and furnishes a copper-liquor of 1·355 spec. grav., and of the following composition :—

	per cent.		per cent.
Cu	3·71	$CoO+NiO$	0·04
Pb	0·01	CaO	trace
Ag	0·005	MgO	0·27
Bi	trace	Alkalies	10·60
$Fe_2O_3+Al_2O_3$	0·29	Cl	12·56
ZnO	4·97	SO_3	8·95
MnO	0·58	$As+Sb$	0·32
Total solids		42·305 per cent.	

After the first lixiviation is over, the dilute condenser-acid, first brought to boiling, is run into the tanks and allowed to act for twenty-four hours; then it is run off, and a third lixiviation effected by dilute sulphuric acid. For 5 tons of ore 2½ cwt. of chamber-acid of 106° Tw., diluted to 12° Tw. and heated to the boiling-point, is employed, and allowed to remain in contact with the ore for two days, or until the liquor acquires a neutral reaction. Its analysis showed :—

	per cent.		per cent.
Cu	0·58	CaO	0·07
$Al_2O_3+Fe_2O_3$	2·13	MgO	0·04
ZnO	0·06	Alkalies	0·62
MnO	0·12	Cl	0·13
$CO+Ni$	0·02	SO_3	2·39
Total solids		6·160 per cent.	

The first copper-liquors contain most of the silver, and are therefore kept apart from the later liquors, poorer in this respect.

The cupric chloride is, of course, easily dissolved in the final liquor; the cuprous chloride in the presence of alkaline chlorides is also dissolved at a higher temperature without difficulty; lastly, cupric oxide should be converted into $CuCl_2$ and Cu_2Cl_2 by the $FeCl_2$ of the final liquor, and become soluble thereby ($2FeCl_2+3CuO=Fe_2O_3+Cu_2Cl_2+CuCl_2$); but this could only be done by an intimate mechanical mixture of the liquor with the ore; and it is therefore preferred to dissolve merely 75 to 80 per cent. of the copper by means of the final liquor, and the remainder by further lixiviations with dilute acids. In Bräuning's paper no hint is given in what way the increase of impurities in the final liquor is prevented. No doubt only a portion of it is taken back into use and another portion run to waste; so that there must always be a partial renewal.

Glendinning (E. P. 8602, 1885) converts the cuprous chloride in the liquors into the cupric salt by blowing in air, in the presence of at least 2 molecules of free HCl to one of salt, together with not less than $3FeCl_2$ to $2Cu_2Cl_2$. [It seems certain that in consequence of this process the solution will require much more iron than before.] If arsenic be present, the excess of free HCl is to be removed by alkali or CuO; in this case, when passing air through the liquid, most of the arsenic will be precipitated in combination with Fe_2O_3.

Rawson (Chem. News, xlix. p. 161) describes a method for estimating cuprous chloride in copper-liquors by means of potassium permanganate.

Precipitation of the Copper from the Liquors.

This is sometimes preceded by a special treatment for obtaining the silver, which will be subsequently described. The precipitation of the copper now takes place everywhere by means of metallic iron, since the ingenious process of Gibb and Gelstharpe has been given up again. The latter consisted in precipitating the copper by sulphuretted hydrogen, which was recovered at a later stage of the process; the precipitated cupric sulphide was washed and pressed in a filter-press, and smelted in furnaces in the usual way into "coarse metal." The acid mother-liquors containing the whole of the sodium sulphate were evaporated to dryness in a furnace, mixed with small coal and reduced in another furnace; thus a mass containing nearly 35 per cent. of sodium sulphide and 2·4 per cent. of sodium carbonate was obtained. This was lixiviated with hot water; the solution was systematically treated with impure carbonic acid, obtained by burning coke; and thus on the one hand sulphuretted hydrogen was given off, which served for precipitating the copper in the first stage of the process; on the other hand a solution of sodium carbonate was obtained, which, after evaporation and calcination, went into the trade as soda-ash. But this process was only applicable to the liquors obtained from the mechanical calcining-furnace (that is, with a minimum addition of common salt); for in the liquors from the ordinary hand-worked furnaces there would be 1 part of NaCl to each 4 parts of Na_2SO_4, which would furnish a very weak soda-ash. This very ingenious process was worked out in all its details, and practically carried out on a very large scale, at the Bede metal-works; but it was given up again, partly because the carbonic acid was too dear, and partly because no furnace-bottom could be constructed fit for resisting the acid liquors for any length of time; partly also because the quality of the soda-ash was too unequal; and finally because the copper was only obtained as sulphide, and had to be smelted at a greater expense than that precipitated by iron.

For this latter process either scrap wrought iron, or scrap cast metal, or "spongy iron" reduced from the residue is employed. Apart from the latter, the thinnest scrap is the best, such as the hoops of cotton or esparto bales; but as light scrap is generally somewhat dirtier than heavy scrap, the copper from the former is rather more impure than that from the latter. The precipitation takes place in wooden tanks exactly of the same kind as those used for lixiviation and furnished with a steam-pipe. They are filled with scrap-iron; copper-liquor is run upon it, and steam is turned on; the heating is continued till a bright strip of iron, held in the liquid, no longer indicates the presence of copper in solution. At Oker, according to the degree of concentration of the liquors, the boiling takes place twice or three times before all the copper is thrown down; the process lasts from one to three days, and requires as much iron as the weight of copper produced, which proves that a large portion of the latter must have been in solution as Cu_2Cl_2. Once a month the precipitated copper is removed from the tanks and washed.

After precipitation, at some works the liquor is passed through a hair sieve in order to separate the copper present in a fine state of division; the copper is washed off the residual iron by a jet of water, or a besom, &c., and left to settle in special tanks. At other works a less rough arrangement is in use, viz. round tubs with wooden agitators, an annular place being fenced off in their upper part for the scrap-iron. The agitation of the liquid causes each part of it to come into contact with the scrap-iron much more quickly, so that the liquids are much sooner freed from copper than in the process first described; besides, the precipitated copper is at once washed off the iron and carried along with the exhausted liquor into settlers, and the process in the precipitating-tubs started again at once, after adding a little more iron.

A continuously acting apparatus for the precipitation of copper has been constructed by Hauch (Dingler's Journal, ccxxiii. p. 286). It consists of a cask revolving round a horizontal axis, provided with ledges inside and filled with iron-borings; copper-liquor is let in, and is speedily exhausted by the rotation of the cask, the copper being at the same time washed off the iron. By combining several casks and systematically allowing the liquor to run into that cask which has been working the longest time, it is possible to obtain a continuous supply of fresh copper-liquor and a continuous running-off of exhausted liquor holding the copper in suspension. Another continuous copper-precipitating apparatus has been described by Kerpely (Wagner's Jahresb. 1877, p. 165).

The precipitation takes place most quickly by employing "*spongy iron*," as is done at the Bede metal-works. This product is made by reducing ferric oxide at so low a temperature that the iron cannot combine with carbon and cannot melt, but remains in the finely divided state, as a "sponge." This method (which may possibly at some time play an important part in the metallurgy of iron and steel) was tried in England for the first time in 1837. Bronac and Deherrypon used it in 1859 for the precipitation of copper, but only in the dry way; but Gossage in the same year introduced the spongy iron in the wet method of copper-extraction. Further patents relating to this subject were taken out by Aas in 1861 and by Bischof in 1862.

Several furnaces have been proposed for this purpose; but only one of them is in use. This is a reverberatory furnace in which the flame, after having passed directly over the charge, returns below the furnace-bed, and thus heats the charge indirectly from below. Figs. 492 to 494 show all the essential details of the furnace. It is, in the drawing, 28 feet 9 inches long; the working-bed has a length of 22 or 23 feet with a width of 8 feet. Dwarf walls, *a a*, 9 inches high, divide it into three compartments, which on one side have two working-doors, *b b*, each. Each compartment is charged and finished by itself. The working-doors are of cast metal, and run air-tight in frames; the same is the case with the fire-door. The fireplace is constructed with a view of generating a reducing flame; the grate has a surface of 4 × 3 feet; and the bearers, *d*, are 3 feet, latterly even 4 feet 8 inches, below the fire-bridge; so that a very deep layer of fuel is obtained, which does not allow any oxygen to get inside the furnace. The furnace-bed is formed

Fig. 492.

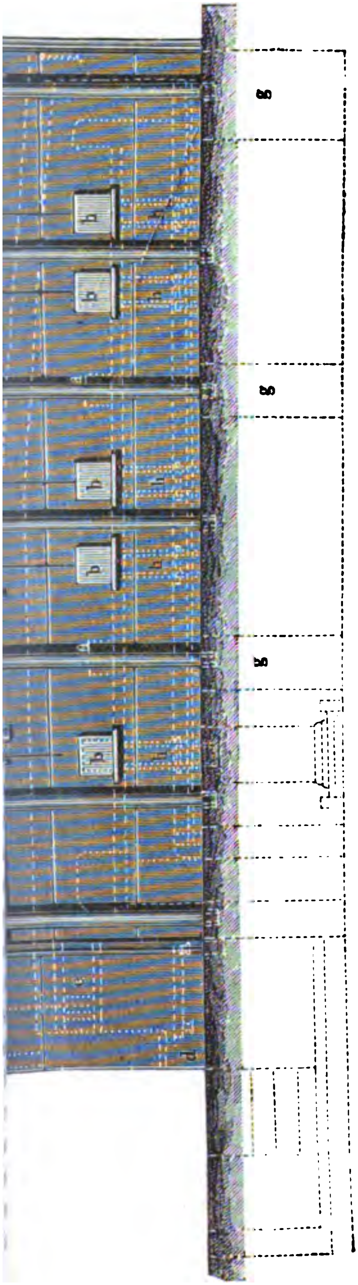
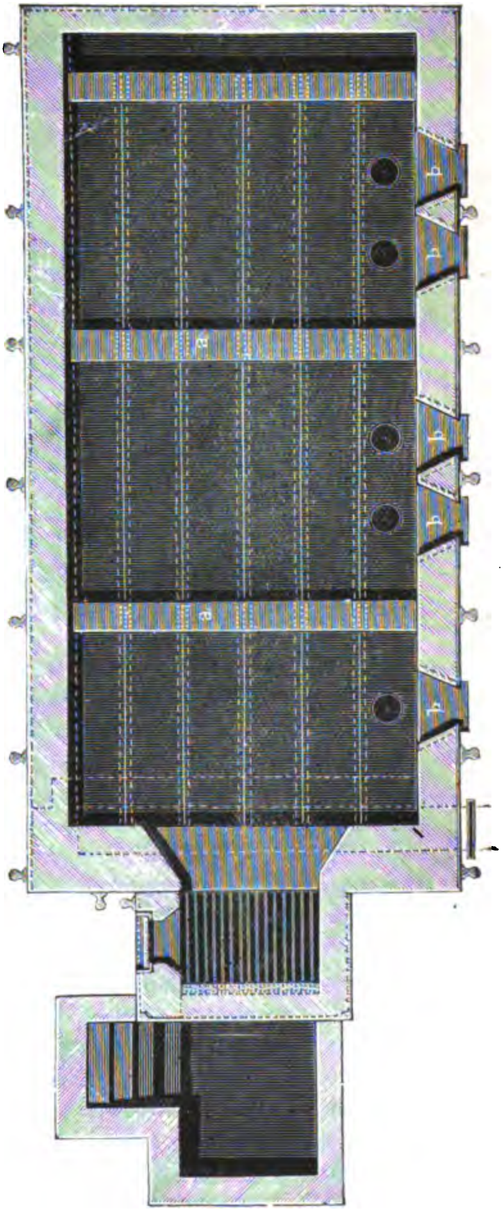
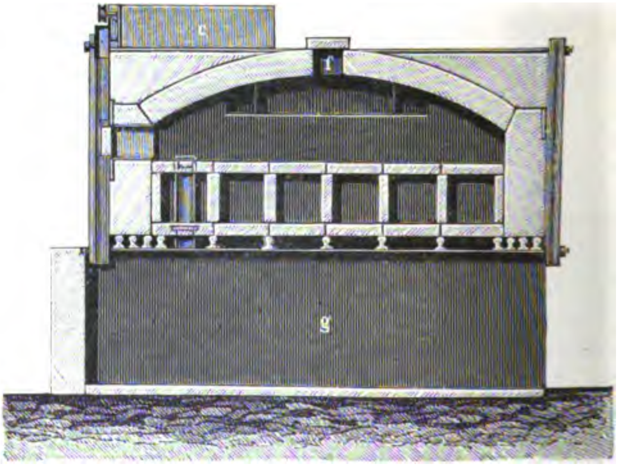


Fig. 493.



by fire-tiles 4 inches thick, with rabbeted edges, partly resting upon the walls forming the divisions of the lower flues, partly upon railway-bars. The flame having travelled through these flues, descends in a vertical shaft along the fire-bridge, and thence goes to the chimney. In this descending shaft there is a fireclay damper, which is closed every time before a working-door or fire-door is opened. The 9-inch furnace-roof is surmounted by a flat cast-iron dish, *c*, supported by short pillars, for drying the ore and mixing it with coal; the mixture is charged into the furnace through the 6-inch pipes *f* carried through the arch. The whole furnace rests on brick pillars, *g*; and the floor on the working side must be so much higher than that on the discharging side that the discharging-boxes can be run underneath the furnace between the brick pillars. The discharging takes place through 6-inch pipes, *h*, descending in front of the working-doors through the furnace-bottom and the lower flues.

Fig. 494.



The discharging-boxes (figs. 495 & 496) are made of sheet-iron, of rectangular section, tapering towards the top. The cover, *a*, is fast, and has in its centre a 6-inch opening with upright flange, *b*, by which the box is connected with the discharging-tube. The bottom of the box is movable, and turns on one side on hinges, whilst the other side is fastened by bolts and cotters. The opening in the cover is easily closed by a metal plate. The whole is mounted on four wheels in such a way that they do not interfere with the movement of the bottom. Each box has a capacity of 12 cubic feet.

When the furnace is at a bright red-heat, it can be charged. Each compartment receives a charge of 20 cwt. dry "purple ore" and 6 cwt. coals, which have passed through a sieve with eight holes to the linear inch. As mentioned, the charging takes place from the cast-iron dish above the furnace-roof. The fire- and working-doors are closed, so that the air enters solely through the coals on the grate, care being taken that the burning mass does not become hollow, lest uncombined oxygen should get inside the furnace. The time of reduction in the compartment nearest the fire-bridge varies from 9 to 12 hours; in the second it is about 18 hours, in the third about 24 hours. The depth of the charge lying on the bed is about 6 inches. During the time of reduction each compartment must be turned over twice, or even three times. Although during this time the damper is closed, a little air always enters the furnace; but the turning-over is indispensable, as the mass would otherwise cake together. The time above stated refers to a bright red-heat; a low red-heat is sufficient for reduction; and the iron thus made is even better for the precipitation of copper; but as in this case much more time is required for reduction (up to 60 hours), this style of working does not pay. The fireplace being so deep, fresh coal need only be thrown in twice or three times every twelve hours, say 15 cwt. for a ton of ore.

Fig. 495.

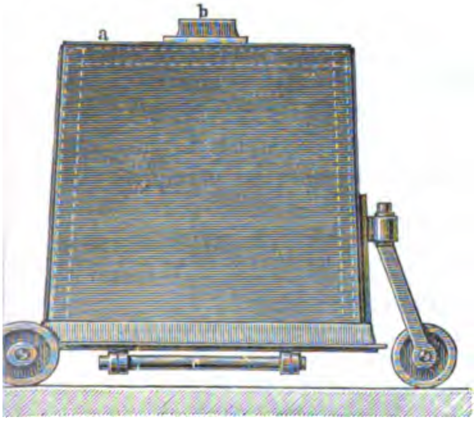
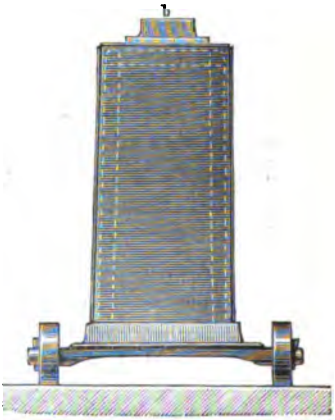


Fig. 496.



The completion of the reduction is ascertained by testing. A small sample is taken out, put on an iron plate, covered with brick till it has become cold, and 1 gram of the (unoxidized) centr part tested by a cupric sulphate solution of known strengt which is run from a burette on to the spongy iron with frequen stirring; from time to time a drop is put on a bright blade of iro to see whether any stain of copper is produced upon it. Whe the reaction in any of the three compartments is finished, th damper is closed; two of the discharging-boxes are run undernea the furnace, and their mouths connected with the discharging-pip by an iron hoop luted with clay; then the charge is raked dow into the boxes as quickly as possible. The boxes are then clos with the loose cover, run out again, and allowed to cool for fort eight hours. They are then lifted by a crane and the cotters a knocked out; whereupon the bottom turns upon its hinges and th whole mass of spongy iron readily falls out, owing to the b tapering upwards. The sponge is then finely ground by a hea edge-runner 6 feet in diameter, and passed through a sieve with fif holes per linear inch; it is now ready for the precipitation o copper.

Two different materials have been proposed for preparing spon iron, viz. pyrites-cinders direct from the chemical works, and th "purple ore" of the copper-works themselves. The followi analyses of average samples gives a clear idea of the chemic difference between them :—

	Pyrites-cinders. per cent.	Purple ore. per cent.
Ferric oxide	78·15	95·10
Iron	3·76	......
Copper	1·55	0·18
Sulphur	3·62	0·07
Cupric oxide	2·70	......
Zinc oxide	0·47	......
Lead oxide	0·84	0·96
Calcium oxide	0·28	0·20
Sodium oxide	......	0·13
Sulphur trioxide	5·80	0·78
Arsenic pentoxide	0·25	......
Siliceous residue	1·85	2·13
	99·27	99·55

Both Bischof and Gossage proposed the direct use of burnt ore for preparing spongy iron, starting from the apparent advantage of utilizing its copper without the trouble of wet extraction. Unfortunately, however, the arsenic contained in the burnt ore remains in the spongy iron, gets into the copper, and greatly injures its quality. G. Bischof, indeed, in his patent of 1862, asserts that arsenic and lead volatilize; Gibb, however, admits this to be the case only for the lead to a great extent, whilst arsenic, being present mostly as arseniates of iron and copper, soon forms stable arseniurets. In fact the spongy iron made direct from pyrites-cinders contains nearly as much arsenic as was originally present in the cinders. On the other hand, the purple ore only retains faint traces of arsenic; it is therefore exclusively used for spongy iron now. The following is an analysis of the spongy iron made in the above way:—

Ferric oxide	8·15	per cent.
Ferrous oxide	2·40	”
Metallic iron	70·40	”
Copper	0·24	”
Lead	0·27	”
Carbon	7·60	”
Sulphur.....................	1·07	”
Alumina	0·19	”
Zinc	0·30	”
Siliceous residue	9·00	”
	99·62	”

According to a later patent (E. P. 8093, 1884), Bischof treats iron oxide with “water gas,” obtained by passing steam over incandescent coke, after having removed any steam from it by cooling. The gas is strongly heated and is passed into the lower part of an inclined retort, into the upper end of which the ore is fed, and allowed gradually to descend to the lower part. Here it comes in contact with the mixed gases, and is reduced to the metallic state by the hydrogen contained in them. The spongy iron so obtained is discharged into a receptacle and cooled before exposure to the air. The remaining gases, deprived as they are of most of their hydrogen, are still combustible, owing to the CO present; they are met in the upper part of the retort by air and are burnt, thus heating the iron oxide preliminary to its contact with hydrogen, and making any external heating in most cases unnecessary. The operation is carried on at a low red-heat.

When spongy iron is employed for the precipitation of copper, continuous stirring is required, for which at some works mechanical agitators are used, at others manual labour; at the Bede metal-works an india-rubber hose, through which a blast of air passes, is moved about in the tank. A Körting's blower would, no doubt, be the best apparatus for this purpose. Perfect mixture is thus obtained; and the precipitated copper only contains 1 per cent. metallic iron, with a great saving of space, apparatus, and labour, as against the work with scrap-iron. However, the greater cheapness of material and treatment in employing spongy iron is bought at the expense of a greater contamination of the copper by unreduced iron oxides and carbon; at the majority of works, therefore, scrap-iron is still preferred. This, of course, depends also on the local price of the latter.

According to Bischof, with spongy iron the arsenic is only precipitated after a few hours, long after the copper has been precipitated, which thus remains free from arsenic. Gibb, however, from many years' experience on the large scale, states that he never found any trace of arsenic in solution after the copper had been precipitated, whichever form of iron or solution of copper might be employed.

The composition of the copper precipitated by the various methods is shown by the following analyses (by Gibb):—

	Precipitated by		
	Spongy Iron.	Heavy Scrap.	Light Scrap.
	per cent.	per cent.	per cent.
Copper	67·50	7·250	67·50
Arsenic	·137	·306	·100
Silver	·011	·046	·066
Lead	1·30	2·60	1·74
Ferric oxide	5·15	4·41	7·56
Carbon	5·10		
Silica	3·20		

At Oker the composition of the copper precipitated by scrap-iron and dried at 100° C. was:—

Cu	77·45	per cent.
Pb	0·63	,,
Ag	0·10	,,
Bi	0·006	,,
As	0·04	,,
Sb	0·15	,,
Fe_2O_3	6·72	,,
Al_2O_3	0·99	,,
Zn	1·02	,,
Mn	0·02	,,
Co + Ni	0·03	,,
CaO	0·10	,,
MgO + Alkalies	2·71	,,
SO_3	4·58	,,
Cl	1·19	,,
Insoluble in acids	0·61	,,
Oxygen + moisture (by loss)	3·654	,,
	100·000	

Copper precipitated from pyrites-cinders made at the Witkowitz works, dried at 100°, was composed as follows (Schneider, Fischer's Jahresb. 1884, p. 163) :—

Cu	11·30	per cent.	together 69·45 Cu.
Cu_2O	65·31	,,	
Ag	0·521	,,	
Au	traces		
Bi_2O_3	0·19	,,	
Fe_2O_3	3·86	,,	
ZnO	0·45	,,	
As_2O_3	1·18	,,	
P_2O_5	0·20	,,	
CuCl	0·32	,,	
$FeCl_2$	0·16	,,	
$CoCl_2$	0·29	,,	
$NiCl_2$	0·07	,,	
$AsCl_3$	1·32	,,	
Carried forward	85·171	,,	

Brought forward	85·171	per cent.
$PbSO_4$	2·19	„
Na_2SO_4	3·39	„
$CaSO_4$	5·32	„
$MgSO_4$	0·59	„
H_2O	2·98	„
	99·641	„

This product is either sent to copper-smelting works or smelted at the wet-extraction works themselves. The copper precipitated from the aqueous solutions, if kept separate from that from the acid solutions, can always be smelted directly for blister-copper by adding to it lime and slags; the copper from the acid solutions is frequently so impure that it has to be mixed with raw ore, or else with soda-waste and slags, and smelted for "coarse metal," which yields blister-copper only after a second roasting. Finally the usual refining takes place. At other works both precipitates are melted together, being charged at once into the furnace in the moist state. The slags produced in this operation, containing from 3 to 10 per cent. of copper, are utilized by smelting them for coarse metal (in a round blast-furnace, 3 feet wide, with four tuyeres), with the addition of soda-waste (calcium sulphide and carbonate). The mass collects in a well, where the coarse metal separates from the slag, and the slag (a "singulosilicate") continually runs off into a bogie. In order that such furnaces may be quickly taken down when the separated iron renders the smelting difficult or impossible, the upper furnace-shaft, together with its jacket, is supported on iron pillars, so that the proper smelting-shaft up to a height of 5 or 6 feet stands quite free within the pillars. The coarse metal here obtained contains about 30 per cent. of copper, and is worked up in the usual way by calcining, smelting, and roasting.

The *furnaces for smelting the copper precipitate* used at English wet-extraction works are reverberatory furnaces of the well-known Swansea type. After smelting, the slag is skimmed off, and the copper tapped as blister. When spongy iron has been used, the excess of carbon prevents the copper from being melted directly to blister; therefore about one half of the precipitate is calcined in large calciners similar to those for roasting burnt ores with salt. Here the carbon is burnt off and the copper partly oxidized; the calcined precipitate is mixed with raw precipitate and smelted, as above, for blister. The blister-copper is refined by roasting to oxidize the iron, sulphur, &c., followed by reducing by charcoal the oxide of copper produced in the roasting, and poling according to the method usually employed by the copper-smelter.

The copper produced is pure and tough. It takes a good place as a marketable article; and its composition in comparison with that of English copper made by the ordinary method of smelting may be judged from the following analyses:—

	Copper from Wet Process.		"English" Copper, Field's Analyses.	
			B.S.	Tough.
	per cent.	per cent.	per cent.	per cent.
Silver	·022	·016	·035	·047
Arsenic	·030	·170	·105	·090
Antimony	none.	trace.	·010	trace.
Bismuth	·006	·019	·035	·130
Lead	none.	·002	none.	—

The complete removal of the arsenic is said to be effected, according to a patent of Bischof's (in 1862), by precipitation with spongy iron—according to a patent of Down's (1870), by almost completely neutralizing the copper-liquors with lime, followed by precipitation with scrap-iron; the foreign metals are said to remain in solution in this case (?). Gibb declares both statements to be entirely erroneous (comp. above, p. 1154); but it is quite possible that in Down's process the arsenic is removed at a previous stage, viz. on neutralizing, as ferric arseniate.

In lieu of precipitating the copper by iron, Weldon (E. P. 5607, 1882) proposed, as a cheaper process, to employ waste chloride of calcium from the Weldon process of manganese recovery or other operations, which produces a mixed solution of copper and sodium chloride, holding calcium sulphate in suspension. The latter is to be separated by filtration, and the copper then precipitated by lime. This process does not seem to have found practical application.

It is unnecessary to say that the copper can be precipitated from its solutions by the electric current, but we cannot enter into this subject in the present treatise.

Höpfner (Germ. pat. 66,096) adds to the copper-liquor so much

NaCl or $CuSO_4$ that the proportion $Na_2SO_4 + CuCl_2$ is attained; then he adds metallic copper, whereby all the copper is precipitated as cuprous chloride, together with the silver in the metallic shape. From the mother-liquor, sulphate of soda is recoverable. Other modifications are also proposed.

Extraction of the Silver contained in Burnt Pyrites.

According to Phillips, the cupreous pyrites-cinders contain on the average 0·0027 per cent. silver and 0·0001 per cent. gold. These metals on calcining with salt are converted into chlorides; and, owing to the solubility of AgCl in NaCl, the silver is found mostly, the gold at least partly, in the liquors obtained by lixiviating the calcined ore. In order to further this, Phillips adds some more common salt in the lixiviating-tanks. These metals are now recovered in most works usually by the process of Claudet (1871). This process consists in precipitating by a soluble iodide the silver from the liquors in the state of AgI, which is quite insoluble in solutions of chlorides. Only the first three liquors (which contain 95 per cent. of all the silver) are employed; the diluted state of the other liquors would make the recovery of the silver from them unprofitable. The liquors, before they undergo precipitation with iron, are completely settled, run into a gauged tank, and their contents of silver accurately estimated by adding to a certain volume hydrochloric acid and a solution of lead acetate, and afterwards potassium iodide. The precipitate is collected on a filter, washed, dried, and fused with a flux of soda, borax, and the finest carbon. The lead regulus obtained is cupellated; and from the weight of the silver thus obtained, that contained in the liquors is computed. To the liquor a solution of potassium or zinc iodide of known strength is now added in sufficient quantity to precipitate all the silver; the iodide solution is diluted to such an extent that it amounts to about $\frac{1}{10}$ the volume of the liquid; the precipitate is allowed to settle; the clear liquor is tested in the laboratory to see if all the silver is thrown down; and if so, it is run into the tanks for precipitating the copper, where it is treated in the usual way. The quantity of iodide employed for the precipitation is much larger than that corresponding to the silver present, since a portion of the lead is thrown down as PbI_2. Probably the silver is precipitated before the lead; but as it is not possible to bring all the silver contained in the liquor into contact with the iodide before the latter has also come into contact with molecules of lead, the precipitate always contains a good deal of lead; so that necessarily a corresponding excess of the precipitant is required.

The precipitate, consisting mainly of AgI, PbI_2, and $PbSO_4$ (which falls down on the liquor cooling), is well washed with water; and if a sufficient quantity of it has been collected, it is treated in the moist state and hot with metallic zinc and a little hydrochloric acid. Thus the AgI and PbI_2 are decomposed completely, the $PbSO_4$ partly, and a liquor containing *zinc iodide* is obtained, which is employed over again for precipitating argentiferous liquors in proportion to its percentage of iodine. On the other hand, a metallic sponge, mixed with pieces of zinc, is obtained having the following composition:—

Ag	5·95	per cent.
Au	0·06	„
Pb	62·28	„
Cu	0·60	„
ZuO	15·46	„
Fe_2O_3	1·50	„
CaO	1·10	„
SO_3	7·68	„
Insoluble residue	1·75	„
Oxygen and loss	3·62	„
	100·00	

This is sent to the silver-works. Usually the argentiferous copper-liquor is first mixed with the solution of ZnI_2 obtained in reducing the AgI &c., and the last portion of the silver precipitated by KI. A certain loss of the latter is unavoidable, whatever care be taken. In this way Phillips obtains about two-thirds of the total silver contained in the burnt ore, and about a similar proportion of the gold; several others have not been content with this, and have given up the process, probably because sometimes on calcining with salt too much Cu_2Cl_2 is formed (its quantity varies from 0 upon 6·70 $CuCl_2$ to 0·62 Cu_2Cl_2 upon 3·75 $CuCl_2$), and in its presence the silver seems to be incompletely precipitated by iodides. At Phillips's works special care is taken to avoid the formation of cuprous chloride; and, perhaps on this account, Claudet's process has been more successful there than elsewhere.

An improvement on Claudet's process is asserted to be offered by the process of E. L. Mayer, patented in 1877. The copper-liquor is precipitated with a solution of glue and KI; the solution contains very much copper and only a few thousandths per cent. of Ag. After the precipitate has settled down, a solution of tannin is added and a little more precipitate obtained. The precipitates are washed with similar dilute acid as serves for dissolving the copper-ores in order to remove the copper they may contain. The acid is neutralized with lime, and treated with alkaline sulphides in a revolving drum till all iodine is removed; the solution containing iodides can be used for again precipitating silver. The remaining sulphides of lead, silver, &c. are to be worked for silver. The addition of glue and afterwards of tannin has for its object to conglomerate the extremely finely divided AgI (of which otherwise a portion would escape collection) into a larger mass.

Another process was proposed in 1873 by W. Gibb. It is based on the observation, that if a copper solution containing very little silver is treated with sulphuretted hydrogen, by far the largest portion of the silver is thrown down as Ag_2S with the first portions of CuS. The H_2S is made from the tank-waste of alkali-works by treatment with dilute hydrochloric acid in wooden vessels; the hydrochloric acid enters the vessel underneath a false bottom made of boards covered with furnace-slags, and runs out near the top completely saturated. The vessels need not be air-tight, as the gas is aspirated from them by an air-pump, the delivery-pipe of which is provided with branches for every one of the precipitating-tanks; an india-rubber hose conveys the gas into these, and, when moved about in the liquid, sufficiently agitates it by the escaping gas. The process is continued until as nearly as possible 6 per cent. of the copper has been precipitated, which generally takes 20 minutes. The bulk of the copper, which otherwise shows on the average 18 ounces of silver per ton, shows after this treatment only 2 to 4 ounces. The 6-per-cent. CuS precipitated at first, however, contains 200 ounces silver per ton. The dilution of the gas by air seems to be favourable to the process. The precipitate is allowed to separate into clear liquor and denser mud; it is washed several times by decantation, and then pressed in a filter-press. The damp sulphides are calcined in an ordinary calciner; the product contains one-fourth of the copper as sulphate, the remainder as oxide or oxychloride, and the silver altogether as chloride. It is roughly ground, washed with water, and the solution of $CuSO_4$, which only contains 1 ounce of silver to the ton of copper, precipitated as usual. The residue, mostly CuO, is systematically extracted by hot concentrated solution of common salt, which dissolves nearly all the silver, leaving only 3 to 4 ounces of silver per ton of copper in the residue. The solution containing the silver is precipitated by milk of lime, the precipitate washed with water to remove the $CaCl_2$, then with dilute sulphuric acid to dissolve the copper, then again with water, and leaves at last a residue containing 9 per cent. of silver as AgCl, worth £700 per ton. It contains besides principally the sulphates of calcium and lead. This treatment is said to cost 9*d.* per ton of burnt ore, and to yield about ½ ounce of silver, of the value of 2*s.* 6*d.*; but, in this shape, it appears to have been given up again.

Chadwick and Jardine, in 1875, patented a new desilverizing process, which is said to be in use at Henderson's works at Irvine. The copper-liquors are diluted to 20° or 25° Tw., and a very weak solution of lead acetate added, which is equivalent to the whole of the Ag, As, Sb, and Bi, less any Pb already contained in the pyrites. Usually about 230 grams of brown sugar of lead per ton are used. On agitating, a light-yellow precipitate is obtained, consisting of 53 per cent. lead sulphate, 5–6 per cent. silver sulphate, and 3 ounces of gold per ton of precipitate (say, 0·01 per cent.). After thorough washing, the gold and silver can be obtained by smelting and refining in the usual way. The copper is said to be thus obtained free from As, Sb, and Bi.

According to a patent of Snelus (1875), finely divided iron dust is to be injected by a blower into the copper-liquors, just sufficient to precipitate 19 per cent. of all the copper; this is said to carry down 80 per cent. of all the silver contained in the solution.

A new patent by Phillips (No. 3923, Oct. 10, 1887) prescribes mixing the copper precipitate with common salt and soda, moistening with water, and grinding in a pug-mill to a paste. The mass is dried and calcined in a reverberatory furnace, constantly stirring, till all the copper has been converted into CuO and all the silver into AgCl. The alkali added decomposes any volatile copper salt present, and almost entirely prevents any volatilization of silver during the calcining-process. The AgCl is extracted from the calcined mass by treatment with a hot solution of common salt. (This is essentially like Augustin's process of 1840, applied to the extraction of silver from ordinary ores.)

Thilo (Chem. Zeit. 1886, p. 822; J. Soc. Chem. Ind. 188 p. 548) gives special prescriptions for estimating the very small quantity of silver (0·003 to 0·008 per cent.) contained in pyrites-cinders.

According to Clemmer (Min. Ind. viii. p. 202, and ix. p. 289 the Claudet process has been entirely given up in the United States. The silver and gold are left in the copper cement, and are paid for at 95 per cent. of their value by the electrolytic refiners as well as by the blue-vitriol works.

Waste Liquors from the Copper Extraction.

Utilization of the sodium sulphate contained in the mother-liquors from the precipitation of copper.—We have mentioned above the process of Gibb and Gelstharpe (p. 1146), which has been given up again. At present the acid mother-liquors are everywhere let run into the rivers, and the sodium sulphate contained in them is lost. At a large copper-works for a time a process was employed by which ferric oxide was simultaneously obtained of great purity and fineness, so that it could be sold on the large scale for red paint. The acid liquors were boiled down to dryness in a brick furnace the residual mass of sodium sulphate and chloride and iron salts was ignited, and ground very fine under edge-rollers; it was then carefully calcined in an ordinary calciner until all the iron salts were peroxidized. The mass was treated with hot water and allowed to settle; the ferric oxide deposited only required washing in order to become marketable as Venetian red. The solution (containing chiefly Na_2SO_4 and NaCl) was concentrated in pans by means of steam circulating in a worm, an agitator preventing the salt from adhering in crusts to the bottom and sides of the pan and to the worm. At a concentration of 1·37 to 1·40 sp. grav. nearly all the sulphate was found to be separated; the liquor with the suspended salt was drained off the precipitate, which was washed with a little hot water and dried in a furnace. It contained only about ¼ per cent. of NaCl, and not a trace of iron; so that it was very well adapted for glass-making. The high price of coals caused the process to be given up at the time; and it does not seem to have been taken up again. Probably the first step, viz. the evaporation of the acid liquors in a brick furnace, would present the same difficulties as in Gibb's process.

Ellis (J. Soc. Chem. Ind. 1884, p. 613) proposed, in lieu of concentrating the liquors by heat, to do so only partially, and then to promote the crystallization of sodium sulphate by cooling. He mentions no trials made on the large scale.

E. de Cuyper (G. P. 53,261 and 54,131) cools the liquor down to —3°, at which temperature all the sulphate of soda crystallizes out, whilst the chlorides of iron, zinc, sodium, &c. remain in solution even at —10° C. After removing the Glauber's salts, the liquor is boiled down to dryness and the residue is calcined; pure ferric oxide is formed and is freed from the zinc chloride by lixiviation.

Jurisch (G. P. 41,737) seeks to utilize the waste liquors after extracting the copper in the following manner:—They are almost neutralized, in tubs provided with mechanical agitators, by means of calcium carbonate; air and steam are blown through, and in the same ratio as ferric sulphate is formed milk of lime is added, without, however, allowing all the acid to be saturated. When all the iron has been precipitated the mud is run into the settlers, the clear liquor is drawn off, and the deposit is passed through a filter-press. It contains some zinc salt, calcium sulphate, and carbonate, and can be made richer in iron by employing it the next time for the saturation of fresh liquor. The basic sulphate of iron thus formed can be employed for making sulphuric anhydride, oxide of iron, paint, &c. The liquor drawn off from it is mixed in an agitator with enough milk of lime to produce basic reaction; the zinc hydroxide precipitated contains some basic ferric sulphate, manganese, and calcium carbonate, and can be utilized in a suitable manner.

According to a communication of the inventor in the 'Chem. Ind.' 1888, p. 3, 50 cubic metres of waste liquor, containing 40 grams $ZnCl_2$ per litre (from pyrites containing 1·5 to 3 per cent. Zn), would yield by his process 806 kil. ferric oxide mixed with calcium carbonate, 3600 kil. ammonium sulphate, 1444 kil. zinc oxide (50 per cent. Zn), 3245 kil. common salt, and a little potassium chloride. This is, however, only derived from analyses and laboratory trials, as Jurisch's process has not found any practical application. It will be interesting, though, to quote from his paper the composition of the liquor he worked with, obtained from the Witkowitz iron- and copper-works, with Hungarian pyrites.

1 litre contained:—

8·6	grams	free	HCl,
73·0	,,	,,	Na_2SO_4,
3·6	,,	,,	K_2SO_4,
16·9	,,	,,	NaCl,
40·3	,,	,,	$ZnCl_2$,
25·9	,,	,,	$FeCl_2$,
3·1	,,	,,	$FeCl_3$,
6·4	,,	other	matters.

He also gives a table of the copper and zinc percentages of a great many descriptions of pyrites.

Wigg, Steele, and Wigg (E. P. 13,722, 1884) mix the waste liquor with waste chloride-of-calcium liquor from the Weldon process in equivalent proportions, when a white bulky precipitate of calcium sulphate is formed, which is filter-pressed and sold as "pearl-hardening." The filtrate is treated with milk of lime, which precipitates ferrous hydrate, and this is oxidized by injection of air or chlorine, washed in a filter-press, and furnaced to yield paint of various shades. Another patent of Wigg's (5620, of 1885) prescribes precipitating the iron by means of ammonium sulphide, and a third patent (11,129, 1885) describes apparatus for these treatments.

Bird's patent (12,458, 1887) seems to contain no essential new feature.

Grabowski (Germ. pat. 71,917) concentrates the liquor by evaporation and crystallization of Glauber's salt to spec. grav. 1·56; he then applies to them an electric current of great intensity, with lead and copper electrodes, by which arsenic and antimony are precipitated as metals at the cathode.

Brewer (Engl. pat. No. 1348, 1895) adds to the liquor a sufficient quantity of calcium chloride solution, separates the resulting solution from the precipitated calcium sulphate (pearl-hardening), removes the silver, and afterwards the iron by calcium carbonate (in the shape of "caustic mud"), then nickel, cobalt, and manganese by bleaching-powder. This treatment practically leaves only the chlorides of zinc and calcium in the solution, which is electrolysed in order to obtain metallic zinc and free chlorine.

Working-Results.

At the Duisburg Works (comp. Hasenclever, Berl. Ber. 1896, p. 2862) the yield from 1000 kil. Rio-Tinto pyrites-cinders is 610 kil. purple ore, 34 kil. copper, 29·5 grams silver, and 0·1 gram gold. As the sale of the large quantities of purple ore is becoming difficult, the Duisburg Copper Company has started to work blast-furnaces of their own.

Clemmer (Min. Ind. viii. p. 202) gives the following calculations of the cost of daily treating 200 tons of mixture of cinders and salts at Natrona :—80 workmen at wages from $1·50 to $2·50, together $134·75 ; unloading cinders and salt, loading purple ore, $35 ; 21 tons salt, $63; pyrites fines, $7 ; 20 tons coal, $20; 5½ tons sheet-iron scrap, $38·50; repairs, depreciation, management, $40: total $338·25, or $1·87 per 2000 lbs. pyrites-cinders.

Other Copper-extracting Processes.

P. Spence (comp. Inspector's Report, 1877–78, p. 48) burns the pyrites (finely ground) in a furnace provided with mechanical stirrers that plough up the ore into ridges, making a change of surface every 2½ minutes (comp. p. 352). He asserts that in this way he burns three tons of ore in a furnace in a day, and renders all the copper soluble to 0·24 per cent. ; thus he is able to wash out the copper salt and avoid the subsequent roasting with common salt. As much as 4·6 per cent. of sulphuric acid is left in the ore, rendering the copper soluble.

H. & Ch. H. Hills (E. P. 1621, 1878) separate the coarse and fine portions of pyrites-cinders by sifting. The fine portions are calcined with salt in the usual manner; the coarse portions are lixiviated with dilute hydrochloric or sulphuric acid, and the copper is precipitated from the liquor by means of iron.

A very similar process of extracting copper from pyrites-cinders has been described by Jetzler (Dingler's Journal, ccxvii. p. 478). He worked pyrites from Borsa-Bánya, in Hungary, containing only 1·01 Cu. The burnt ore decays easily on lying in the air; and after sifting off the not decayed core through a sieve with 10 meshes to 1 centim. square, the copper can be extracted by hot weak hydrochloric acid of 3°–4° Tw.; probably ferric chloride acts here, chlorinating the lower sulphides of copper, and being reduced to $FeCl_2$. On washing, solutions of 24° Tw. are obtained, which besides copper, contain Ag, Pb, $Al_2(SO_4)_3$, &c. The metals were precipitated by scrap-iron; and the precipitate was sold to a smelting-works according to its value of Cu and Ag. The process did not pay very well, as the residue could not be used as an iron-ore.

Another process was patented (in 1873) to Baron Leithner in Austria (Dingler's Journal, ccxi. p. 349). The burnt ore (in this case containing about 1 per cent. of copper) is to be smelted with 36 per cent. calcium hydrate in a kiln heated by the waste gas of a blast-furnace; the product is to be smelted for pig-iron, which now contains 2·09 per cent. Cu, and this is to be used for precipitating copper; so that its own copper is utilized as well.

Some patents of Mason's (Nos. 2984, 2992, and 2993, 1877 seem to contain nothing new of any importance.

The whole of the processes connected with the wet extraction of copper, as far as published up to the end of 1878, and including many proposals or actually employed processes not mentioned here (because they do not refer specially to the treatment of pyrites-cinders from sulphuric-acid works), are described in a condensed form by Bode (Dingler's Journal, ccxxxi. pp. 254, 357, 428).

The patents of Hargreaves and Robinson (E. P. 5601, 1886, and 3704, 1887) for extracting gold, silver, and copper from pyrites can be only briefly mentioned in this place.

Mr. John Hargreaves informs me of the following results, obtained in 1887 by this process. He treats the pyrites-cinders, obtained in the usual manner, in a closed chamber with fire-gases and excess of air, in order to burn all the residual sulphur; the mass is allowed to cool down to the point were no cupric chloride can be volatilized, and is then treated with gaseous HCl till it is sufficiently decomposed. It is then lixiviated with water in tanks, after being moistened with strong hydrochloric acid; the residual ferric oxide is obtained in lumps, which are immediately ready for the blast-furnace.

The cinders originally employed contained, according to the size of the grain, from 1·00 to 1·09 per cent. Cu in a shape soluble in water, 0·71 to 1·09 soluble in hydrochloric acid, 1·61 to 2·79 insoluble. They were passed through a sieve with 7 meshes per linear inch, and chlorinated as above described. The average from the upper part of the chamber then tested 3·90 per cent. Cu soluble in water, 0·63 soluble in weak hydrochloric acid, 0·56 insoluble; from the lower part of the chamber 3·51, 0·77, and 0·28 per cent. respectively. The treatment for burning the residual sulphur lasted from 26 to 96 hours, the chlorination from 24 to 72 hours. The liquors contained pretty much silver and a little gold; the washed residue contained only 0·8 to 0·12 per cent. copper. (I am not aware whether this process is now actually at work or not.)

Chase (G. P. 120,277) mixes ground pyrites-cinders with a little carbonaceous material, roasts the mixture at a full red-heat with access of air, mixes the product with a quantity of salt corresponding to the amount of copper present, and then continues the process in the ordinary way.

Treatment of very poor Cupreous Cinders.

The case now occurs much more frequently than formerly, that ores containing only one or two per cent. of copper are burned. In such cases the cinders are too poor to apply the treatment described above, pp. 1117 *et seq.*, beginning with roasting the ground cinders with salt; on the other hand there is too much copper left in them to meet the demand of the iron-smelter. To overcome this difficulty the acid treatment, mentioned in some of the processes described, p. 1165, is applied. Frequently the cinders are previously exposed to the air for some time, in order to render some of the copper soluble in water; sometimes they are put in the leaching-vats quite fresh and warm. It depends upon the nature of the ore which of these two ways is preferable, and it must be found by experience in every practical case.

The acid treatment takes place in lead-lined wooden boxes, provided with a false bottom, and is carried on as described, pp. 1139 *et seq.*, beginning with weak liquor from a previous operation, to which is added a little sulphuric acid, two or three per cent. of the weight of the cinders. This acid liquor is left in contact with the cinders for two days; the strong liquor thus formed is then run off into the precipitating-tank and is replaced by weaker washings and ultimately by fresh water, so that the operation is finished in seven or eight days. The weak washings formed are pumped back into other leaching-tanks by means of injectors. The copper is precipitated in lead-lined vats by means of scrap-iron, suspended in wicker baskets or otherwise, temperature of 50° or 60° C. The precipitated copper mud is to iron-smelters, or is roasted into oxide in reverberatory fur and dissolved in hot weak sulphuric acid, to manufacture sulphate.

By this treatment it is hardly possible to extract all the but sufficiently so to render the cinders fit for the blast-furna

General.

According to Hunt's 'Mineral Statistics' for 1874, p. 65, existed in Great Britain in that year 22 copper-works for extraction, which together consumed 329,000 tons of burn (say, equal to 450,000 tons of pyrites). Two of them sulphate of copper; three went as far as refined copper; others sold their precipitate to copper-smelting works. The production of copper from this source in 1874 amounted to tons. In 1882 the quantity of burnt ore worked for copper 434,427 tons, containing 15,300 tons of copper.

On laying out a copper-extraction works the levels mu carefully attended to, so that the very large quantities of substances and liquors may be easily moved about. At Ol Hebburn, &c. all the apparatus are arranged at different le The design of the Oker works has been published by Bräu (comp. the quotation on p. 1118). The top level is occupied the charging-loft; to which the burnt ore and the salt are bro by bogies; attached to it are two edge-runners, each of grinds daily 15 tons of ore and 2¼ tons of salt down to a siz 2 millims. The mixture is taken by bogies to the furna situated at a little lower level; the furnaces are heated by producers, situated still lower down. Below the furnaces th follow, at three descending levels, the lixiviating-tanks, precipitation-tanks, and cisterns for the "final liquor," which it is pumped up again by injectors and used for lixivi fresh ores.

CHAPTER XIV.

APPLICATIONS OF SULPHURIC ACID AND STATISTICS.

THE *principal applications* of sulphuric acid are the following:—

I. In a more or less *dilute* state (say from 144° Tw. downwards). For making sulphate of soda (salt-cake) and hydrochloric acid, and therefore ultimately for soda-ash, bleaching-powder, soap, glass, and innumerable other products. Further, for superphosphates and other artificial manures. These two applications probably consume nine-tenths of all the sulphuric acid produced. Further applications are:—for preparing sulphurous, nitric, phosphoric, hydrofluoric, boric, carbonic, chromic, oxalic, tartaric, citric, acetic, and stearic acids; in preparing phosphorus, iodine, bromine, the sulphates of potassium, ammonium, barium (*blanc fixe*), calcium (*pearl-hardening*); especially also for precipitating baryta or lime as sulphates for chemical processes; sulphates of magnesium, aluminium, iron, zinc, copper, mercury (as intermediate stage for calomel and corrosive sublimate); in the metallurgy of copper, cobalt, nickel, platinum, silver; for cleaning (pickling) sheet-iron to be tinned or galvanized; for cleaning copper, silver, &c.; for manufacturing potassium bichromate; for working galvanic cells, such as are used in telegraphy, in electroplating, &c.; for manufacturing ordinary ether and the composite ethers; for making or purifying many organic colouring-matters, especially in the oxidizing mixture of potassium bichromate and sulphuric acid; for parchment paper; for purifying many mineral oils, and sometimes coal-gas; for manufacturing starch, syrup, and sugar; for the saccharification of corn; for neutralizing the alkaline reaction of fermenting liquors, such as molasses; for effervescent drinks; for preparing tallow previously to melting it; for recovering the fatty acids from soap-suds; for destroying vegetable fibres in mixed fabrics; generally, in dyeing, calico-printing, tanning, as a chemical reagent in innumerable cases; in medicine against lead-poisoning, and in many other cases.

II. *In a concentrated state.* For manufacturing the fatty acids by distillation; purifying colza oil; for purifying benzene, petroleum, paraffin oil, and other mineral oils; for drying air, especially for laboratory purposes, but also for drying gases for manufacturing processes (for this, weaker acid also, of 140° Tw., can be used); for the production of ice by the rapid evaporation of water in a vacuum; for refining gold and silver, desilvering copper, &c.; for making organo-sulphonic acids; manufacturing indigo; preparing many nitro-compounds and nitric ethers, especially in manfacturing nitro-glycerine, pyroxyline, nitro-benzene, picric acid, and so forth.

III. *As Nordhausen fuming oil of vitriol* (*anhydride*). For manufacturing certain organo-sulphonic acids (in the manufacture of alizarine, eosine, indigo, &c.); for purifying ozokerite; for making shoe-blacking; for bringing ordinary concentrated acid up to the highest strength as required in the manufacture of pyroxyline and other purposes.

Statistics.

I have calculated the production and consumption of sulphuric acid in the *United Kingdom,* mostly from official sources (Chem. Ind. 1884, p. 213), on the following basis:—From the amount of pyrites imported follows the total quantity of acid made on the basis of 130 H_2SO_4 for each 100 pyrites. The quantity of salt decomposed, taking 7 salt=4 pyrites, or 100 salt=75 H_2SO_4, gives the quantity of acid decomposed for this purpose. The remainder will have been used mostly for manure-making, taking the acid used for other purposes as being derived mostly from brimstone. All acid is calculated as monohydrate.

Year.	Acid made from pyrites.	Used for decomposing salt.	Pyrites-acid used otherwise.	Brimstone-acid made.	Total acid made.
	tons.	tons.	tons.	tons.	tons.
1878	747,900	417,406	330,494	124,271	872,171
1879	716,625	445,265	271,360	126,884	843,509
1880	771,771	501,612	270,152	133,653	905,424
1881	736,797	475,724	261,073	115,599	852,396
1882	806,793	472,151	334,642	134,742	941,535
1883	815,574	484,252	331,322	125,064	940,638

These statistics are probably wrong in an important part, viz. the amount of brimstone-acid made. Owing to the total want of information on the quantity of brimstone burnt for acid-making, I assumed all the brimstone imported into England to be used for this purpose, leaving the sulphur recovered from alkali-waste and otherwise produced in England for the remaining uses (lucifer-matches, gunpowder, &c.). But this is probably allowing far too much, for in the 25th Alkali Report (for the year 1883), where for the first time the quantity of brimstone burnt for sulphuric acid is mentioned, it is stated = 17,925 tons, which would yield about 51,300 tons of H_2SO_4. Hence the quantity of brimstone-acid in the foregoing table should be reduced by about 70,000 tons per annum, and that of the total acid made by the same figure.

The number of sulphuric-acid works under Government inspection in England and Ireland in the year 1889 amounted to 221, including those in which the acid was entirely used up at the works themselves for alkali, manure-making, &c. In Scotland this number was 32. In 1899 the figures were, 175 works in England and Ireland, 24 in Scotland; in 1901, 172 works in England and Ireland, 24 in Scotland. Only 2 of these worked the contact-process.

There are no direct statistics for the production of sulphuric acid in the United Kingdom obtainable, but we can come pretty near the truth by utilizing the figures for the production and importation of pyrites given on p. 42. We cannot estimate the quantity of acid made from brimstone, native or recovered, zinc-blende, spent oxide of gas-works, and from H_2S in the manufacture of sulphate of ammonia, which must altogether amount to a considerable quantity, but not very large in comparison with that made from pyrites. Assuming a yield of 134 parts real H_2SO_4 from an average Spanish pyrites, and taking account of the difference between the metric and English ton, we arrive at the following figures for pyrites-acid, expressed as real H_2SO_4, made in Great Britain :—

Year.	Tons.	Year.	Tons.
1888	820,200	1895	781,400
1889	864,600	1896	789,300
1890	880,400	1897	835,500
1891	873,800	1898	877,800
1892	811,000	1899	939,800
1893	822,300	1900	992,400
1894	826,300		

The quantity of brimstone-acid will be hardly larger than in 1883, *i. e.* about 50,000 tons, and the acid made from other sources may furnish another 50,000 tons or more.

The official statistics gave the following for the production of sulphuric acid in *Germany* :—

In the year	1879	185,106	tons
,,	1882	286,953	,,
,,	1885	343,294	,,
,,	1886	325,722	,,
,,	1887	347,529	,,
,,	1888	399,938	,,
,,	1890	460,081	,,
,,	1891	512,100	,,
,,	1892	538,500	,,
,,	1893	575,800	,,
,,	1894	617,900	,,
,,	1895	608,900	,,
,,	1896	668,900	,,
,,	1897	768,200	,,
,,	1898	768,243	,,
,,	1899	832,667	,,
,,	1900	849,900	,,
,,	1901	856,827	,,

These figures are unfortunately of very little value; up to 1881 they comprise only the acid made in metallurgical establishments, after that the total acid, including that used up at the works for alkali-making, superphosphates, &c. Up to 1886 "Englische Schwefelsäure," calculated as acid of 140° Tw., and Nordhausen O.V. were enumerated separately; from 1887 the figures do not distinguish between acid of 106°, 140°, 168°, and Nordhausen acid!

The production of sulphuric acid in Germany has been pretty accurately estimated by Hasenclever (Chem. Ind. 1884, p. 78) for the year 1882 as follows:—

Ore used.	tons.	Sulphuric acid of 142° Tw. made. tons.	Equal to H_2SO_4. tons.
German pyrites	130,892	183,249	142,934
Spanish pyrites	55,000	90,750	70,785
Hungarian, Norwegian, &c. pyrites	9,000	13,950	10,881
Mixed ores at Oker, Freiburg, Mansfeld	...	40,200	31,356
Zinc-blende	...	30,000	23,400
		358,149	279,356

The same author (Chem. Ind. 1899, p. 25) quotes the German production in 1898 as follows :—

	Acid of 142° Tw. tons.
Made from 55,183 tons German pyrites...	80,015
„ „ 332,004 „ foreign „ ...	571,046
„ „ zinc-blende	136,868
„ at Freiburg, Oker, and Mansfeld from mixed ores	50,738
„ from gas-oxide	6,915
	845,582 = 659,554 tons real H_2SO_4.

This is estimated on the basis of a yield of 143 parts acid 142° Tw. on 100 parts German pyrites, or 172 on 100 Spanish pyrites.

In 1900 the importation of sulphuric acid into Germany was 20,634 tons, the exportation 37,738 tons. In 1902, 22,205 tons were imported, 477,666 tons exported.

The quantity of *fuming* sulphuric acid produced in Germany is stated = 4685 tons in 1897, 14,092 tons in 1898, 19,526 tons in 1899; but this seems to include only that acid which came into the market, not that used up in the factories themselves for the manufacture of tar-colours, &c.

Since, in 1901, 488,632 tons pyrites were imported into Germany, or 156,000 more than in 1898, we may, on the assumption that the other raw materials did not undergo an essential change, estimate the quantity of real H_2SO_4 made in Germany in 1901 = 878,000 tons. This equals the production of the United States, and nearly approaches that of the United Kingdom.

In 1900 there existed in Germany 75 sulphuric-acid works, 17 of which made acid only as a secondary product. The number of men employed was 3798. Upwards of ten factories worked the contact-process.

France in 1867 made 90,000 tons, in 1877 150,000 tons, in 1889 234,000 tons acid (what strength?), in 1899 (Monit. Scient. 1900. p. 561), in 54 works, about 800,000 tons acid of 52° B. = 492,000 tons H_2SO_4 *.

The Société St. Gobain now has 17 works in France and 1 in Spain. The 15 works already existing in 1899 possessed 250,000 cub. metres chamber-space (= nearly 9 million cubic feet), and produced 480,000 tons sulphuric acid (chamber-acid). It had 22 platinum stills of a value of £120,000.

Austria in 1902 imported 12,460 tons sulphuric acid, and exported 9451 tons. In 1902 four works had introduced the contact-process. The total amount of sulphuric acid manufactured was about 200,000 tons, strength not mentioned (Z. angew. Ch. 1903, p. 215).

Belgium in 1899 produced 210,000 tons acid of 60° B. = 164,000 tons H_2SO_4. About 60 per cent. of this was made from blende, 40 per cent. from pyrites.

Italy in 1879 possessed 10 sulphuric-acid works, most of them of small size, producing 7140 tons of acid of 106°, 2210 tons of 172°, and 2520 tons of 168° Tw.; say, altogether, 9883 tons H_2SO_4. Since that time the production of sulphuric acid has very largely increased. In 1895 Candiani (Chem. Ind. 1895, p. 153) stated the total chamber-space of the Italian factories = 108,000 cubic metres, which, if they were fully at work, would be equal to a production of at least 65,000 tons H_2SO_4 per annum. A statement by Chiaraviglio, "from official sources," according to which Italy, in 1900, produced 220,000 tons acid, calculated as H_2SO_4, seems very doubtful.

According to Zsch. f. angew. Ch. 1903, p. 117, there was produced in Italy:—

	In 1900. tons.	In 1901. tons.
Sulphuric acid (strength not stated) ...	229,555	235,172
Sulphur dioxide (liquid)	1·4	13·5
Nitric acid....................................	2,071	2,069

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* This estimate is probably too high, looking at the figures for production, importation, and exportation of pyrites given p. 50.

Russia produced, according to official information (Chem. Ind. 1900, p. 542), in 1899 about 100,000 tons sulphuric acid from 50,000 tons pyrites (about 12,000 tons of which was mined in Russia) and 16,500 tons sulphur. Great part of this is made at Baku for the chemical treatment of petroleum products. The importation of sulphuric acid from other countries is but slight: about 500 tons in 1894, 280 tons in 1895, 220 tons in 1896, 165 tons in 1887.

The import duty for ordinary sulphuric acid is 22 kopeks (gold) per pud = about £2 3*s*. per ton*. The selling-price varies from 0·75 to 1·00 rubel per pud for strong acid, about 0·60 rubel for chamber-acid, 0·40 rubel for "black acid" (recovered from the acid-tar of petroleum refineries by diluting with water, removing the tar, and concentrating the aqueous portion by evaporation).

According to Chem. Zeit. 1901, p. 313, formerly all sulphuric acid in Russia was made from Sicilian sulphur, of which even in 1898 16,000 tons were imported. Now the pyrites found in the Ural Mountains, containing up to 7 per cent. copper, has largely come into use. Of this 16,000 tons is obtained per annum, and another 33,000 tons is imported from Scandinavia and Spain.

Fedetijew (Zsch. angew. Chem. 1902, p. 865) estimates the Russian consumption of Sicilian sulphur at 20,000 tons per annum, of Russian pyrites at 30,000 tons; in 1901 73,600 tons pyrites were imported from Spain, Portugal, Sweden, and Norway. The amount of acid produced is about = 125,000 tons H_2SO_4, and about 1000 tons 30 per cent. fuming acid. The factories are situated at Wiatka, Kasan, Baku, St. Petersburg, Riga, Moskow.

For the *United States* we possess unusually good materials for statistics in a Report made by the Washington Census Bureau (United States Census Bulletin, No. 210). In the original the quantities are quoted in pounds weight and the costs in dollars per short ton (of 2000 lbs.). I reduce them in the following to *long* tons (of 2240 lbs.) both for quantities and costs; and I also give the equivalent of the quantities in real monohydrate (H_2SO_4).

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* For fuming acid or anhydride = 1 rubel (gold) per pud = about £9 18*s*. per ton.

In the year 1890 there were 105 establishments making sulphuric acid, which produced

Acid of 50° B. tons.	Value per ton. dols.	Acid of 60° B. tons.	Value per ton. dols.	Acid of 66° B. tons.	Value per ton. dols.
450,832	7·62	9098	10·77	158,274	16·37

equivalent in H_2SO_4:

=279,515	6186	144,612

Grand total=430,313 tons H_2SO_4; value 7,679,473 dols.

In the year 1900 there were 127 establishments (with only 28 chemists !), which produced

Acid of 50° B. tons.	Value per ton. dols.	Acid of 60° B. tons.	Value per ton. dols.	Acid of 66° B. tons.	Value per ton. dols.
875,392	7·46	15,635	12·92	336,856	14·29

equivalent in H_2SO_4:

=542,743	10,632	309,907

Grand total=863,282 tons H_2SO_4; value 14,247,185 dols.

[This does not seem to include the acid made from zinc-blende and other smelting-operations, which, according to Eng. Min. Journ. August 1902, p. 182, in 1900 amounted to 75,650 long tons of 66° B.]

Of the 127 works reporting in 1900, 31 burned brimstone only, 79 pyrites only, 17 both brimstone and pyrites. (Nothing is said about blende.) The data given in the original do not admit of stating what quantities of brimstone and pyrites were consumed respectively, but these are quoted from other sources in pp. 24 and 58. The Report abstracted here gives as the average production of 20 works a production of 402 lbs. acid of 50° B. [say, 62 per cent. H_2SO_4] from 100 lbs. brimstone, with a consumption of 4·29 lbs. nitre, and 234 to 160 lbs. (average 204) acid of 50° B. from 100 lbs. pyrites, with a consumption of 1·2 to 2·5 lbs. of nitre per 100 lbs. pyrites. [The yields here quoted, mechanical averages from very discrepant sources, possess of course very little practical value. The statistics given by Gilchrist in Journ. Soc. Chem. Ind. 1899, p. 460, are rendered obsolete by the above official report.]

Japan in 1900 consumed about 28,000 tons sulphuric acid 50° B., mostly from native pyrites. Nearly 10,000 tons of this were consumed by bleaching-powder works, 8500 tons by petroleum refiners; over 1000 tons were exported, partly to China (Journ. Soc. Chem. Ind. 1900, p. 299). This statement contrasts very much with that given below.

In Chem. Zeit. 1902, p. 1231, we find a report on the manufacture of sulphuric acid in Japan by Professor T. Nishigawa, of which we give a short abstract. The first works was erected in 1872 for the Imperial Mint at Osaka by an Englishman, Mr. Kinder, in the old-fashioned style of burning brimstone on plates without towers. These were followed by similar works in 1880. In 1883 Nishigawa erected the first factory on modern principles, and many others followed, principally at Osaka and Tokio. Several of these have reached a daily make of 80,000 to 100,000 lbs. acid of 50° B. They are built on thoroughly modern principles, with Gay-Lussac and Glover towers, partly also with Lunge towers. Since 1895 brimstone has been partly replaced by pyrites. Except the first, all of them have been constructed by Japanese chemists, and they are all managed by Japanese. There are now nine acid-works, producing nearly 50,000 tons pure H_2SO_4 per annum.

ADDENDA.

(Up to August 1st, 1903.)

P. 14. *Brimstone as raw material for sulphuric-acid making.*—According to the Alkali Inspector's Report, No. 38, p. 50, a large brimstone-acid factory was erected in Ireland in 1902, without Gay-Lussac tower.

P. 15. *Boiling-point of sulphur.*—Holborn and Grüneisen have found this by a very exact method $=444^{\circ}\cdot 8$ of the hydrogen scale (Drude's Ann. 1901, vi. p. 123).

P. 20. *Exportation of sulphur from Sicily in* 1901 *and* 1902.—The following figures are taken from Chem. Trade Journ. 1903 xxxii. p. 203. The figures for 1901 quoted in Min. Ind. x. p. 596 and in Chem. Ind. 1902, p. 586, do not differ very much from them.

Exports to:	1901. tons.	1902. tons.
United States and Canada...	141,617	168,919
France	74,384	67,249
Italy.............................	74,517	45,603
United Kingdom...............	22,403	25,477
Russia	15,110	17,295
Portugal	11,335	10,614
Germany	23,447	25,906
Austria..........................	18,842	19,080
Greece and Turkey......... ..	21,701	20,548
Belgium	7,462	12,323

Exports to:	1901. tons.	1902. tons.
Scandinavia	24,485	24,918
Spain	2,979	2,249
Holland	10,858	8,648
Other Countries	9,889	18,484
Total	459,030	467,319

Bolis, in Chem. Ind. 1902, p. 586, states the total production of brimstone in Italy in 1901:—

	tons.
District of Bologna	21,269
„ „ Naples	7,306
„ „ Caltanisetta (Sicily)	534,543

From the latter 69,963 tons were exported to continental Italy.

P. 21. *Sulphur in Transsylvania.*—A large deposit of native sulphur is reported to have been found in the Borgó Alps (Chem. Ind. 1903, p. 147).

P. 21. *Sulphur in Greece.*—Sulphur-ore exists on the island of Milo, where it is used in the raw state for dusting the vines. About 1000 tons are extracted in the pure state and are used for the manufacture of sulphuric acid.

P. 22. *Sulphur in Japan.*—In 1900, 14,435 tons were produced, especially in the provinces of Hokkaida, Rikuzen, Asumi, and Shenaro. In 1901, 10,705 long tons were exported to the United States.

P. 23. *Sulphur in North America.*—In 1901 the production in the United States amounted to 6867 long tons, derived from Nevada, Idaho, Utah, and Louisiana, in order of the importance of their output. The importation of crude sulphur into America in 1901 was 174,194 tons (most of it being used in the manufacture of sulphite pulp for paper-making); besides 748 tons flowers and 268 refined. The price at New York in 1901 oscillated between 19·92 and 23·30 $ per long ton.

P. 29. *Sulphur from sulphides.*—Swinburne (G. P. 134,734) places the sulphate ore in a bath, formed of fusible chlorides of heavy metals, heats to a high temperature, and applies the electric current, which produces free chlorine from the chloride. The chlorine decomposes the sulphide with liberation of sulphur, wh distils off, metallic chloride being reformed.

P. 30. *The World's production of sulphur* in 1900, accord to Min. Ind. x. p. 593, was :—

	long tons.		long to
Austria *	862	Japan	14,435
France *	11,551	Russia	?
Hungary	123	Spain	750
Germany	1,445	Sweden	70
Greece	891	United States	4,701
Italy	544,119		

Comp. p. 30 concerning the sulphur extracted from Lebl soda-waste, which is not included in the above.

P. 31. *Analysis of crude sulphur*.—F. B. Carpenter (Jou Soc. Chem. Ind. 1902, p. 832) has met with crude sulphur fr Mexico containing so much gypsum that carbon disulphide d not extract all the sulphur. This can, however, be done, or t sulphur approximately estimated, by burning, after extracting t calcium sulphate by boiling with hot hydrochloric acid. T moisture must be estimated by drying in a vacuum over sulphur acid.

P. 31. *Detection of arsenic and selenium in sulphur.*—St (Chem. News, vol. lxxxvi. p. 135) declares the method of Schæp for the detection of arsenic in sulphur to be erroneous. E proceeds as follows :—He extracts 200 grms. of the sample dur two hours in a paper filter in the Soxhlet apparatus with carb disulphide, withdraws the paper filter, allows the CS_2 to evapora scrapes out the residue, heats this with 50 c.c. strong nitric a till all acid is driven off, adds 1 c.c. strong hydrochloric acid a after a few minutes, 5 c.c. warm water, filters into a test-tu washes the insoluble residue with a little water, adds to the solut 20 c.c. strong hydrochloric acid, 1 or 2 c.c. of a fairly concentrat solution of stannous chloride in hydrochloric acid, and, last 3 c.c. of strong sulphuric acid, heats gently and allows to sta over-night. If As or Se (insoluble in CS_2) is present, a d brown precipitate is formed. This is filtered through asbes (purified by aqua regia), washed and dried at 100°, transferred a hard glass tube, 7 mm. bore, closed at one end; the tube is th drawn out immediately above the contents to 1·5 mm. bore for a length of about 80 mm. The bulb portion, containing the asbestos, &c., is heated to redness in a Bunsen flame. As and Se are driven off and condense in the narrow part of the tube. Se appears both in the black and red modification and is at once identified by its characteristic odour; As is found by heating the sublimate in a current of air, when As_2O_3 forms a ring of glistening crystals, or, in the presence of traces of water, globules of a solution of oxide. If no selenium is found here, it may be sought for in the CS_2 solution, by distilling off the CS_2, oxidizing the mass of sulphur by means of fuming nitric acid [no mean task with 200 grams sulphur !], filtering through asbestos, evaporating the filtrate till strong white fumes of sulphuric acid appear, and then reducing with $SnCl_2$, &c., as above.

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* Raw sulphur-ore of very varying percentages.

P. 33. *Grinding and sifting sulphur.*—A. Walter (G. P. 136,547) performs these operations in an atmosphere of inert gas which is made to circulate through the apparatus. In this way the formation of sparks is avoided, and the sulphur can be reduced to such a degree of fineness that it passes through a sieve of 5000 meshes per square centimetre.

P. 33. *Examination of sulphur for fineness, &c.*—H. Fresenius and P. Beck (Zsch. analyt. Ch. xlii. p. 21) draw attention to some points necessary to observe. The Chancel test for the degree of fineness should be made with ether distilled over sodium. After shaking up all agitation should be avoided; the sulphurimeter should be fixed in a stand and at once immersed in water of 17°·5 C. Organic matter and ashes should be estimated at little over 200° C. after evaporating the sulphur. The microscope will show whether a mixture of ground sulphur and flowers of sulphur is present. The temperature in estimating the water by drying should not be above 70° C. The authors found in several samples of Sicilian sulphur from 0·02 to 0·26 per cent. ashes, 0·02 to 0·05 per cent. organic substance, 0·17 to 0·64 per cent. residue insoluble in CS_2, of which 0·13 to 0·28 was sulphur, and 0·16 to 0·405 per cent. insoluble in caustic soda solution spec. grav. 1·2.

P. 45. *In Germany the importation of pyrites* in 1901 was 488,632 tons, the exportation 23,680 tons; in 1902, 482,095 tons were imported, 35,370 tons exported.

P. 45. *Pyrites in Austria.*—At Davidsthal, in Bohemia, pyrites is found containing 49 per cent. S with 6 per cent. carbon. It is used only for manufacturing SO_3 by the contact-process.

P. 57. *Pyrites in America.*—In 1901 the production was 234,8 long tons, including 7585 tons "coal-brasses" from Ohio. Th pyrites came from Virginia, Colorado, Massachusetts, and New Yor named in the order of production. The importation of pyrit was 403,706 tons, the total consumption of pyrites in the Unit States (part of it for the manufacture of sulphite pulp) 638,5 tons. Min. Ind. x. p. 596 draws attention to the fact that lar and hitherto unused stores of zinciferous sulphur-ores exist in th States of Arkansas, Missouri, Kentucky, and Kansas.

P. 53. *Spanish pyrites.*—Recently hundreds of thousands tons of "leached ores" have come into the market, especially Ri Tinto and Pomaron. These ores are exposed to the weather and the washed with water, in order to extract the copper, of which the retain only 0·3 to 0·5 per cent. They test 49 or 50 per cen sulphur in the dry state, but they generally contain about 5 per cen water. In the pyrites-burners they make very much dust, a they are very porous and friable.

P. 59. *World's production of iron-pyrites.*—According to Mi Ind. x. p. 598 this was in 1900:—

	Metr. tons.
Belgium	400
Prussia	1,700
Canada	36,316
France	305,073
Germany	169,447
Hungary	87,000
Italy	71,616
Newfoundland	33,000
Norway	95,000
Portugal	345,330
Russia	25,000
Spain	356,018
Sweden	179
United Kingdom	12,484
United States	204,538
Total	1,743,111

This does not include the very large quantities of cupreou pyrites (over 1 per cent. Cu) obtained in Spain and Portug (comp. footnotes to p. 59).

P. 77. *The estimation of carbon in pyrites* is described by Treadwell and Koch (Zsch. angew. Ch. 1903, p. 852).

Pp. 89 & 367. *Sulphuric acid from hydrogen sulphide.*—According to 'Iron Age,' July 10, 1902, the H_2S developed as a by-product in the refining of asphaltum at the works at Ventura, Cal., is burned to SO_2 and converted into sulphuric acid in lead chambers. The present production is 10 tons of high-grade acid daily.

P. 93. *Nitrate of soda in California.*—In the Mohave Desert, 80 or 100 miles from Manvel, in Bernardino and Inyo counties, on the Santa Fé Railway, a large deposit of rich nitre-earth has been discovered. According to Eng. & Min. Ind. 1903, p. 186, about 21 million tons are visible, but this figure is likely "to be revised." It will be two or three years before this property is in a condition to supply the market.

P. 93. *Nitrate of soda, statistics.*—According to Journ. Soc. Chem. Ind. 1902, p. 1002, the consumption of nitrate of soda during the year ending June 30, 1902, was as follows:—United Kingdom 111,000 tons; Continent 897,000 tons; United States 185,000 tons; the whole World 1,209,000 tons. The price on June 30, 1892, was 8*s*. 9*d*. per cwt.

Germany in 1901 imported 529,568 tons and exported 13,480 tons.

P. 98. *Hydrates of nitric acid.*—H. Erdmann (Zsch. anorg. Ch. xxxii. p. 431) has isolated in a crystallized state the following hydrates of nitric acid:—

Orthonitric acid $N(OH)_5 = 63{\cdot}63$ per cent. HNO_3. Melts at −35°, stable at −15°, boils under a mercurial pressure of 13 mm. at 40° to 40°·5, with dissociation.

Eight-basic nitric acid $(HO)_4N-ON(OH)_4 = 68{\cdot}87$ per cent. HNO_3, analogous to crystallized arsenic acid or the tetracalcic phosphate forming "Thomas slags." Extremely viscid. This is the acid which remains on prolonged boiling of nitric acid of various strengths. Melts at −39° C.

Three-basic nitric acid.—$O=N(OH)_3 = 77{\cdot}78$ per cent. HNO_3. Melts at −34°.

Four-basic nitric acid.—$(HO)_2NO-O-NO(OH)_2 = 87{\cdot}52$ per cent. HNO_3. Melts at −65°·2; boils under a pressure of 15 mm. at 48°.

P. 114. *Nitric-acid retorts.*—According to notes from actual practice, the nearly cylindrical middle part of the Guttmann retorts (see fig. 20) lasts practically for ever. The bottom parts may la up to 10 years, the covers about one year. The latter ar surrounded with a sheet-iron rim and serve for drying the nitr [In would seem preferable to me, on the contrary, to avoid a condensation inside the covers by protecting them against coolin by brickwork or otherwise, and to effect the drying of the nit by means of the waste heat from the retort fires.] Each retor receives a charge of 12 cwt. nitre and 13 cwt. sulphuric ac (95 per cent.), which is worked off in 14 hours with only 1 cwt. coal. After cooling for 6 hours the nitre-cake is run off and th retort is ready for charging again. A set of 10 retorts is worke by two shifts of three men each; the men have also to wheel th nitre from the storehouse and to manage the condensation.

P. 131. *Condensation of nitric acid.*—Bate and Orme, of th National Explosives Company, have patented the following im-provements of the "water battery" (B. P. 25,790, Nov. 2 1902). The object is: to ensure more efficient circulation of th condensing water; to enable a defective pipe to be removed an replaced without interfering with the other pipes, and to avo reducing the strength of the acid if a pipe should crack or lea while the charge is being worked off. Each vertical condensin pipe, or as many of them as may be necessary, is surrounded by separate water-jacket, which in case of a crack or leak may b rapidly emptied. The condenser otherwise resembles a Guttma water-battery, but is claimed to be superior to this in the abov mentioned respects. These water-jackets are made of lead; the are open at the top and are fused to the lead covering of th wooden frame holding the pipes in their places, and they are ma to hold water by means of a gland ring and rubber joint ring circular section. The specification gives all details of the co struction of the water-jackets and other parts of the apparat It has been successfully at work for some time at the Hay Explosive works, where the process is as follows:—The vapou issuing from the retorts described on p. 114 pass into an inclin stoneware conduit, with a glass bulb in the middle, and the into a series of five stoneware pipes, about 5 feet long and 4 inch wide each, connected alternately at top and bottom. The fi three of the set are converted into Liebig coolers by means of ope topped lead-jackets, about 8 inches wide, fed with cold water at t bottom. The last two pipes are left uncovered and are mer cooled by the air. These five pipes communicate at the bottom by a Guttmann "chamber-pipe," or in any other suitable way, with a pipe conveying the condensed strong acid into a closed receiver, placed outside the building. The inlet-pipe is fixed tightly in the receiver and is provided with a side tap through which, during the last stage of the operation, the weaker acid condensed then is run into another receiver. In these vertical pipes the acid-vapours are almost entirely condensed to strong acid. The remainder passes through six ordinary receivers, charged with 6 inches of water, which is left there until the specific gravity amounts to 1·42 or 1·43. Lastly, the gases from four retorts pass into a Lunge tower fed with a little water. By pumping back the weak acid formed here it may be brought to specific gravity 1·40. All the acid from the six receivers and the weak acid condensing in the pipes towards the end of the operation, which altogether amounts to about 5 per cent. of the total, is put back into the retort in a subsequent operation, so that the *whole* of the acid is eventually obtained of spec. grav. 1·507=92 per cent. HNO_3, inclusive of 1 to 1·2 per cent. N_2O_4. This amounts to 97 per cent. of the theoretical quantity. 2 per cent. of the nitrate is left undecomposed in the nitre-cake; this admits of conducting the separation in such a manner that the residual nitre-cake retains enough water to obtain all the nitric acid in the strong state, as stated above. It is entirely free from sulphuric acid, chlorine, and iron. The 12 cwt. nitre charged yield 8$\frac{3}{4}$ to 9 cwt. strong nitric acid, no weak acid at all leaving the process. This should be contrasted with the Valentiner process, which in one distillation furnishes only 80 per cent. of the acid in a strong state.

Guttmann has recently described a modification in details of his condensing-battery (Germ. pat. No. 136, p. 679).

P. 131. Plath (E. P. 9133, 1901) makes *clear concentrated* nitric acid by interposing between the perpendicular cooling-pipes and the receiving-vessel a cooling-worm about 80 feet long, air being passed through opposite to the current of acid, and the temperature in the cooling-tub being regulated in such a manner that the acid comes out both cold and free from lower nitrogen oxides.

P. 139. *Utilization of nitre-cake.*—Barbier (U.S. P. 487,546, 1892) proposes treating a solution of 35° to 45° Baumé by refrigeration to about 10° C.; in this case a decomposition takes place into crystallized neutral sulphate of soda and free sulphuric acid [?].

P. 139. *Utilization of nitre-cake.*—Cheeseman (U.S. P. No. 714,145, Nov. 25, 1902) describes a process which I long ago proposed to those interested in the matter as open to everybody, viz., neutralizing a solution of nitre-cake by lime (or calcium carbonate), separating the calcium sulphate by filtration or otherwise, running off the solution of sodium sulphate and utilizing this for instance for the manufacture of "blanc fixe," by precipitation with barium hydrosulphide solution.

P. 141. *Recovery of nitric acid from waste acid of nitroglycerine and nitrocellulose works.*—The following process, as carried out at Hayle, works very well indeed. The waste acid is denitrated in a small Volvic column, standing in a strong leaden socket, with an overflow about 8 inches from the bottom. The steam-pipe must not end free in the column, but *within the liquid*, say 6 inches below its level, so that the steam rising from the liquid effects the denitration. The operation is commenced by putting water into the lead socket and passing in steam until the column is hot. Only then the feeding with waste acid is started and is conducted in such a manner that at the bottom sulphuric acid of 74 to 75 per cent. H_2SO_4 issues at a temperature of 160° C., in which case the denitration is perfect. The nitrous vapours pass first through four empty receivers, for the purpose of cooling, then successively through five Lunge towers, about 6 feet high, and then through eight receivers, charged with 6 inches of water each. The towers are fed very slowly with water, the holes in the covers being plugged up with wood in such a manner that the water trickles in in drops. On the top of the first tower one of the holes is left open in order to draw in the necessary air. Thus the towers yield nitric acid of 57 to 64 per cent. HNO_3, inclusive of 1·5 per cent. N_2O_4, on the average of spec. grav. 1·40. The water in the receivers is left there until the specific gravity reaches 1·37. This plant denitrates 10 tons of waste acid per diem.

P. 144. *Production of nitric acid from atmospheric air.*—Bradley and Lovejoy (Engl. pat. 8230 of 1901; U.S. P. 709,867 and 709,868 of Sept. 30, 1902) produce nitric acid from atmospheric nitrogen by means of an electric arch divided into thin subdivisions so as to obtain a large surface for small electric energy. Their process is carried out by the Atmospheric

Products Co., at Niagara Falls. Their apparatus is described in ‘Electrochemical Industry’ (Philadelphia), vol. i. p. 20.

Muthmann and Hofer (Berl. Ber. 1903, p. 438) have scientifically investigated the combustion of nitrogen into nitric oxide in the electric flame; also Lepel, *eod. loc.* 1897, p. 1027, and 1903, p. 1251.

Great hopes are entertained in some quarters concerning the preparation of nitric acid by cheap electricity, but the economical aspect of this question is as yet anything but clear, and so far no method is known of obtaining *concentrated* nitric acid in this way.

P. 144. *Manufacture of nitric acid from ammonia.*—Ostwald (Addition, dated April 9, 1902, to Fr. Pat. 317,544; comp. E. P. 698 and 8300, 1902) gives the following additional prescriptions. The air must be in considerable excess, the temperature of reaction must exceed 300° C.; the passage of the gaseous mixture must be as rapid as possible, and the gases are previously heated by the hot gases coming away from the contact-mass. The apparatus consists of an open tube, charged at one end with the contact-material (platinum coated with platinum sponge), fixed air-tight in a cylinder with its open end projecting. The cylinder has an aperture close to the exit end for admission of the gases, which thus pass along the sides of the tube before entry through the end containing the contact-material. The gases, strongly heated by the reaction, heat the tube on their passage onwards, such heat being in part taken up by the entering gases.

P. 149. *Sesquioxide of sulphur* S_2O_3.—According to Witt (Chem. Ind. d. deutsch. Reiches, p. 118) this substance, the anhydride of thiosulphuric acid, obtained by dissolving sulphur in fuming sulphuric acid, is preferable to all other reagents as a powerful reducing-agent (in sulphuric-acid solution) in the manufacture of naphtazarin and several other cases.

P. 154. *Acid-smoke.*—A book, comprising the whole of this subject, has been published by Haselhoff & Lindau, under the title ‘Die Beschädigung der Vegetation durch Rauch’ (Leipsic, 1903).

P. 179. *Specific gravities of sulphuric acid.*—A. Marshall (Journ. Soc. Chem. Ind. 1902, p. 1509) gives a table of specific gravities of sulphuric acid, calculated for weighing in the air at $\frac{15^\circ}{15^\circ}$ C. It is based on Pickering’s work of 1890, which to some extent deviates from the results obtained by myself with Naef &

Isler. I have shown in Zsch. f. angew. Ch. 1890, p. 569, that the very narrow basis on which Pickering's elaborate figures rest is much too uncertain to attribute to his results greater accuracy than to ours.

Marshall founds upon the same table a method for estimating the strength of sulphuric acid (*loc. cit.* p. 1511), which, owing to the necessity of corrections for the impurities, cannot vie with an ordinary titration either in speed or in accuracy.

P. 187. *Influence of impurities on the specific gravity of sulphuric acid.*—Marshall (*loc. cit.* p. 1508) shows that sulphuric acid, recovered from the waste acid of nitrating processes, may contain notable quantities of nitric acid, which make the specific gravity of strong sulphuric acid appear higher than normal. Mixtures of both acids up to 7·5 per cent. HNO_3 showed an increase of specific gravity up to 1·862; from that onwards the specific gravities decrease. Further experiments showed that an additional 0·1 per cent. of various sulphates raises the specific gravity of strong sulphuric acid by 0·001; lead sulphate by 0·0015; As_2O_3 by 0·0013; nitrosulphuric acid by 0·00027. Lead sulphate is much more soluble than stated by Kolb (*suprà*, p. 190); acid of 98 per cent. may contain 0·09 per cent. $PbSO_4$, acid of 94 per cent. 0·06 per cent. $PbSO_4$.

Pp. 203 and 875. *Action of sulphuric acid on platinum.*—Contrary to the ordinary statement in chemical text-books, Conroy (J. Soc. Chem. Ind. 1903, p. 465) has found that sulphuric acid, even when pure, exerts a marked solvent action upon platinum. In fact the quantity taken up by acid of 95 per cent. H_2SO_4 at 250° C. far exceeds that observed in practice. This is explained by the fact that reducing-substances, like As_2O_3, S, SO_2, and even N_2O_3, retard the solvent action. Nitric acid does not promote it directly, but in practice it is injurious because it oxidizes the reducing-substances present. Ammonium, ferrous and ferric sulphate, sodium chloride and nitrate have no action. The greater destruction observed when bringing the acid to higher concentration is not due to that concentration itself, but to the higher temperature necessary for it.

P. 243. *Analysis of fuming sulphuric acid.*—Grünhut (Zsch. f. analyt. Chem. 1899, xxxviii. p. 167) has drawn up a table which admits, by the addition of two figures, to reduce percentages of H_2SO_4 calculated to 0·01 per cent. into percentages of SO_3.

P. 248. *Detection of arsenic in sulphuric acid.*—According to Dawdow (Chem. Cbl. 1895, i. p. 811), Rosenheim (Chem. News, lxxxiii. p. 277), and Berry (Journ. Soc. Chem. Ind. xx. p. 322) *selenium* interferes with the Marsh test. Schindelmeiser (Chem. Cbl. 1902, ii. p. 960) found that no AsH_3 is given off until all selenium has been precipitated by zinc or aluminium in the Marsh apparatus. Selenium, either as seleniate or selenate, also forms precipitates with potassium iodide very similar to AsI_3, so that Seybel and Wikander's test is also interfered with.

P. 248. *Detection and approximate estimation of minute quantities of arsenic.*—Although the minute rules laid down by the Arsenic Committee of the London Section of the Society of Chemical Industry (Journ. Soc. Chem. Ind. 1902, p. 94) refer to the examination of beer, brewing-materials, food-stuffs, and fuels, we shall reproduce here that portion of them which can be applied also to the examination of sulphuric acid. The Committee recommend to apply the Marsh-Berzelius test.

1. *Pure reagents.*—To half a litre of "pure" sulphuric acid a few grams of sodium chloride are added and the mixture is distilled from a non-tubulated retort, the first portion of about 50 c.c. being rejected. One volume of the distilled acid is diluted with four volumes of water. Zinc is obtainable free from arsenic. It should be regranulated by melting it and pouring it from some height into cold water. Mr. A. H. Allen holds it to be essential that the zinc should contain a trace of iron.

2. *Apparatus.*—A bottle or flask, holding about 200 c.c., is fitted with a doubly-bored cork, india-rubber stopper, or with a ground-in glass connection, carrying a tapped funnel holding about 50 c.c. and an exit-tube. The latter is connected with a horizontal drying-tube, containing, first a roll of blotting-paper soaked in lead-acetate solution and dried, or a layer of cotton-wool prepared in a similar way, then a wad of cotton-wool, then a layer of granulated calcium chloride, and finally a thick wad of cotton-wool. To this tube is fitted a hard glass tube, drawn out into a thin tube of such external diameter that at the place where the arsenic mirror is expected the tube just passes through a No. 13 Birmingham wire-guage (=0·092 inch). A good Bunsen flame is used to heat the wider part of the hard glass tube close to the constriction. About one inch of tube, including the shoulder, ought to be red-hot. A piece of moderately fine copper gauze

(about one inch square), wrapped round the portion of the tube to be heated, assists in insuring an equal distribution of heat.

3. *Mode of testing.*—About 20 grms. of zinc are placed in the bottle and washed with water to clean the surface; all parts of the apparatus are connected and sufficient acid is allowed to flow from the funnel so as to cause a fairly brisk evolution of hydrogen. When the hydrogen flame (which during the heating of the tube should be kept as uniformly as possible a quarter of an inch high burns with a round (not pointed) top, all air has been removed from the apparatus. The Bunsen burner should then be placed under the hard glass tube, as described, and more acid (10 to 20 c.c. run in as required. With good materials no trace of a mirror is obtained within half an hour. Great care must be taken that, when additions of acid are made to the zinc, no bubble of air is introduced, since in presence of air the arsenic mirror may become black and uneven, whilst it should be brown.

Should the blank experiment not be satisfactory, it must be ascertained, by changing the materials methodically, whether the fault lies with the acid, the zinc, or the apparatus.

4. *Preparation of standard mirrors.*—A hydrochloric-acid solution of arsenious oxide, containing 0·001 mgrm. As_4O_6 per c.cm., is prepared by diluting a stronger solution with distilled water. 2 c.c. of this solution are introduced into the apparatus. If the zinc is "sensitive," a distinct brown mirror is obtained within 20 minutes. (Some "pure" zinc is, from a cause at present unknown, not sensitive.) The portion of the tube containing the arsenic should be sealed off while still filled with hydrogen. Mirrors are similarly made with 0·004, 0·006, 0·008, and 0·01 mgrm. of arsenious oxides. The first stage of every test must be blank for at least 20 minutes.

Arsenic in both states of oxidation can be detected and estimated by the procedure described.

The proof that the mirrors are arsenical is obtained as follows:—The narrow portion of the tube containing the mirror is cut off, the hydrogen replaced by air, and the ends sealed up. The tube is then repeatedly drawn through a Bunsen flame until the mirror has disappeared. On cooling, minute sparkling crystals of arsenious oxide deposit, which can be readily identified under the microscope. With this test quantities of 20 c.c. will give an indication in the presence of 0·0000 15 per cent., or 1 part arsenious oxide in 7 millions.

I have thought it right to quote this method; but (as with some which follow) it is really *too* delicate for the purposes of the acid-maker, from whom it cannot be demanded that his "purified" acid should contain less than 1 part As_4O_6 in 200,000 of sulphuric acid. It is acknowledged on most sides that acid containing such a minimum of arsenic can be employed even for the purpose of manufacturing glucose, tartaric acid, and so forth.

Bertrand (Bull. Soc. Chim. [3] xxvii. No. 16; Chem. News, lxxxvi. p. 191) concentrates the arsenic in not more than 30 to 60 c.c. of liquid in the hydrogen apparatus. The oxygen is entirely driven out of the apparatus, after putting in the zinc, by pure CO_2 taken from a bottle of liquid CO_2; this takes only a few minutes. Then one or two drops of dilute platinum chloride in 10 c.c. of dilute sulphuric acid (1 : 5) is added, and after ten minutes the arsenical solution is introduced. The gas is dried by cotton-wool, previously heated to 120° C. It is passed through perfectly clean glass tubes, which are chosen all the narrower the smaller the quantity of arsenic expected; *e. g.* only 1 mm. wide, if less than $\frac{1}{300}$ mgrm. is present. The end is drawn out very fine for several centimetres, about 10 or 15 cms. from the place where the ring is to be formed. A space of about 20 cms. length of this tube is heated to nascent redness. If the tube is thin nothing else need be done; if it is of thick glass, a space of the above length should be confined on both sides by a band of filtering-paper kept moist, so as to prevent the ring from spreading too fast. In this way one-thousandth of a milligram or even less can be detected; but of course the greatest care must be taken not to introduce it by the reagents. Such exceedingly slight mirrors must be kept from oxidizing by sealing the tube while filled with hydrogen.

Parsons and Stewart (Journ. Amer. Chem. Soc. 1902, xxiv. p. 1005) show that in the presence of iron some arsenic is retained in the Marsh-Berzelius flask, and hence iron should be avoided if quantitative results are required.

For the Reinsch test very detailed prescriptions are given by A. H. Allen in Journ. Soc. Chem. Ind. 1901, p. 281, and by the Manchester Brewers' Association, ibid. p. 646; but these also refer to beer, glucose, &c.

A third test, proposed by Gutzeit, is frequently preferred on account of its simplicity. It consists in allowing hydrogen, containing arsenic, cooled as in the Marsh test, to act upon solid silver nitrate, deposited by drying on a piece of blotting-paper. Convenient forms of apparatus for this test have been constructed by Kirkby (J. Soc. Chem. Ind. 1901, p. 281), by Tyrer (ibid. p. 282) and by Dowzard (ibid. 1900, p. 1145). Comp. also Hehner (ibid. 1901, p. 194), Bird (ibid. 1901, p. 390), Richardson (ibid. 1902, p. 902), and Gotthelf (ibid. 1903, p. 191).

For sulphuric acid specially Bettendorf's test is also employed, in which a solution of stannous chloride in its own weight of strong hydrochloric acid is added to the solution to be tested. In the presence of arsenic a brown colour and, later on, a black precipitate are formed, much more quickly when heating. According to Messel (J. Soc. Chem. Ind. 1901, p. 192) 0·01 mg. As_4O_6 can be detected in 1 c.c. sulphuric acid by this test.

The detection of arsenic has been most thoroughly treated in a Report of a Committee appointed by the Commissioners of Inland Revenue, of which Professor T. E. Thorpe was Chairman. They recommend, in the first instance, Bloxam's electrolytic method for the reduction of the arsenic to arseniuretted hydrogen, which has been worked out in the Government Laboratory. The apparatus serving for this is illustrated and minutely described in the Report. It is somewhat costly, and of course only applicable where an electric current of sufficient intensity is available. Therefore in many cases the zinc method will be preferred, in spite of its drawbacks. This method, as described in the Report, agrees in most respects with the prescriptions laid down by the Arsenic Committee of the Society of Chemical Industry (*suprà*, p. 1190); the deviations comprise only some certainly not unimportant details. The size of the apparatus employed and the amount of zinc and acid are much smaller, the rate of evolution of the gas is less, and the arsenic is deposited over a smaller area of glass (Journ. Chem. Soc. vol. lxxxiii. p. 974; Journ. Soc. Chem. Ind. 1903, p. 965).

P. 349. *Herreshoff furnaces.*—In 1902 there were over 300 of these in America. In Europe there were 103, of which 44 were at work, 59 building; viz. 26 in France, 25 in Germany, 16 in Scandinavia, 14 in Italy, 6 in Great Britain, 4 in Russia, 3 in Austria, 3 in Spain, 3 in Holland, 2 in Roumania, 1 in Belgium. Of these 43 serve for the contact-process, 38 for the lead-chamber process, 19 for sulphite wood-pulp, 3 for liquid sulphur dioxide. They are stated to give no trouble whatever with granular ores;

but much more so with dusty ores, especially the "leached ores," p. 1182. Even these cause difficulties only in the lead-chamber process; they require 1½ times as much dust-chamber space as ordinary hand-furnaces for smalls and sometimes mechanical draught. In the case of contact-processes and of wood-pulp they can be applied without reserve, since the gases must be, anyhow, thoroughly washed for these purposes. [Opinions respecting these furnaces are still very much divided, as proved by various attempts at overcoming the dust difficulty.]

P. 364. *Mechanical furnaces for blende.*—In Eng. & Min. Journ. 1900, p. 261, a description of Zellweger's furnace is given, the principal peculiarity of which is a roller-shaped stirrer. It turns out 30 tons in 24 hours.

P. 456. *Cooling the gases in chambers.*—Pratt (U.S. P. 715,142, Dec. 2, 1902) cools the chambers, towers, flues, or conduits by a cooling medium without bringing them directly into contact with the latter; also the hot uncombined gases, which are then passed again into the chamber.

P. 477. *Reaction-towers.*—Rabe (Zsch. angew. Ch. 1903, p. 437) makes general observations on the principles on which modern towers are constructed. He also describes a feeding-arrangement with automatic movement and arrangements for internal cooling of such towers.

P. 499. *Pipe-towers.*—Hart and Bailey (J. Soc. Chem. Ind. 1903, p. 473) describe a plan exactly similar to Hacker and Gilchrist's pipe-towers, only of somewhat larger dimensions. They found a cooling-action of nearly 40° C., an increase of production of 60 per cent., and a decrease of nitre of from 3·5 down to almost 2·0 per cent. All this agrees perfectly with the views first clearly stated by the author of this book. The acid scrubbed out in their pipe-towers contained practically no nitre. [They state the strength of this acid to vary between 90° and 120° Tw., but they do not distinguish between the reactions shown by the lower and the higher of these strengths. While at the lower strength no "nitre" could be retained, it is inconceivable that acid of 120° Tw., condensed from the vesicular to the completely liquid state in an atmosphere of nitrous fumes, should not contain any nitre!]

P. 509. An instrument for *mechanically calculating the weight of sulphuric acid in the chambers* is described by C. Davidson in

Chem. News, lxxxvii. p. 205 (also Journ. Soc. Chem. Ind. 1903, p. 625).

P. 543. The *introduction of water as spray* (in the "atomized" form) is strongly advocated by Kestner, especially according to Benker's plan, described in the text of this book (J. Soc. Chem. Ind. 1903, p. 334).

P. 560. *Fan-blasts for producing draught in chambers.*—Petschow (Zsch. angew. Ch. 1903, p. 12) quotes some misadventures with fans made of stoneware. Plath (ibid. p. 159) and Niedenführ (p. 161) controvert his statements and prove the success of such fans. As built by the Vereinigte Thonwaarenwerke, of Charlottenburg, they perform a duty of 120 cub. metres or 4200 cub. feet per minute. Petschow (ibid. p. 304) practically yields the point.

Kestner (J. Soc. Chem. Ind. 1903, p. 333) strongly advocates the use of fans for working acid-chambers. He prefers placing them at the end of the system, between two Gay-Lussac towers.

Niedenführ (G. P. 140,825, March 27, 1902) places a fan between two Glover towers, the first serving mainly for concentration, the second for denitrification.

P. 573. *The measurement of the velocity of a current of gas* can be carried out by measuring the pressures before and behind a throttling arrangement interposed in the conduit-pipe. On this principle is constructed the instrument of Dr. H. Rabe (G. P. 111,019) described in Zsch. angew. Ch. 1900, p. 236; 1901, p. 950; 1903, p. 136.

P. 618. Kestner (J. Soc. Chem. Ind. 1903, p. 337) discusses various systems of *automatic acid-elevators.*

P. 734. *Path which the gases travel in the chambers.*—Porter (J. Soc. Chem. Ind. 1902, p. 476) describes experiments made with a glass model of a chamber in which he produced a visible smoke. His experiments, which were certainly made under conditions widely differing from those existing in an acid-chamber, are in practical agreement with the ideas specified in the text.

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ERRATUM.

Page 214, line 7, *read* trioxide (*not* tetroxide).

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